



TITLE:

Mechanistic Study on the One-Electron Reduction of Carbonium Ions(Dissertation_全文)

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CITATION:

Komatsu, Koichi. Mechanistic Study on the One-Electron Reduction of Carbonium Ions. 京都大学, 1974, 工学博士

ISSUE DATE:

1974-05-23

URL:

<https://doi.org/10.14989/doctor.k1493>

RIGHT:



MECHANISTIC STUDY
ON THE ONE-ELECTRON REDUCTION
OF CARBONIUM IONS

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DEPARTMENT OF HYDROCARBON CHEMISTRY
FACULTY OF ENGINEERING
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Chapter 1 General Introduction

The carbonium ion has been long considered to exist only as a transient species (i.e., a reaction intermediate) in various types of organic reactions. On the other hand, a rapid development in modern organic chemistry in the last two decades has enabled us to isolate, in a purely crystalline state, a variety of carbonium ions with either classical or non-classical structure. The study on the physical and chemical properties of these "stable" carbonium ions has attracted much interest among the chemists in the fields of both theoretical and applied chemistry. However, it seems that the chemical studies concerning these carbonium ions have been mainly focused on their ionic reactions and that the homolytic reaction, i.e., a transformation of the carbonium ion to the organic radical by one-electron reduction, has received comparatively less attention in spite of its significance as one of the most essential reactions from both the synthetic and mechanistic standpoints.

Although the reactivity scale of carbonium ions in one-electron reduction in gaseous phase has received considerable theoretical interest in association with the ionization potential of organic radicals to carbonium ions,¹⁾ relatively little attention has been given to the reducibility scale

in solutions. Furthermore, the range investigated of carbonium-ion structure is quite small. Heretofore, the electrochemical method has been applied for the quantitative assessment of the reducibility of the stable carbonium ions in solutions. The polarography has been conducted on the tropylium²⁾ and triarylcyclopropenium ions,³⁾ and polyarylmethyl cations,^{2c, 4)} in both aqueous and non-aqueous media. Also, the cathodic reduction of the tropylium ion⁵⁾ and the triphenylmethyl cation⁶⁾ have been performed on a preparative scale. A more quantitative study has been carried out by the measurement of the reversible electrode reduction potentials of the equilibrated solutions of triarylmethyl cations and the corresponding radicals.⁷⁾

However, in these electrochemical methods, there is a severe limitation in the carbonium-ion structure and also some special technique is required for the observation of the "reversible" reduction potentials.

On the other hand, there are some qualitative studies reported on the chemical reduction of carbonium ions in solutions. The reductants employed in these studies are classified into the inorganic species, i.e., metals and low-valent metallic ions, and the organic species, either neutral or anionic, including organometallic compounds.

In a series of their systematic investigation, Conant and his co-workers⁸⁾ first demonstrated that the vanadous and chromous ions readily reduce various types of diaryl- and triarylmethyl cations including some xanthy

cations. Ever since, the chromous ion has been widely employed in the reduction of organic halides,⁹⁾ but examples of the chromous-ion reduction of the well-defined carbonium ions are confined to the qualitative studies reported on the reduction of the triphenylmethyl cation¹⁰⁾ and the tropylium, pyridinium and pyrylium ions.¹¹⁾

Among the metallic reductants, zinc powder has been most frequently used, for example, to reduce the substituted tropylium,^{12, 13, 14)} cyclopropenium,¹⁵⁾ pyrylium,^{16, 17)} thiopyrylium,^{18, 19)} and pyridinium²⁰⁾ ions, since a facile reduction of the tropylium ion to give bitropyl was found by Doering and Knox.²¹⁾ Metals with the higher ionization tendency, such as potassium,²²⁾ sodium-potassium alloy,²³⁾ and sodium amalgam²⁴⁾ have been applied for the generation and ESR measurements of radicals of the tropyl^{22, 23)} and pyridinyl²⁴⁾ systems.

As for the organic one-electron reductants, olefinic compounds such as vinyl alkyl ether²⁵⁾ and tetraphenyl-p-xylylene²⁶⁾ have been reported. In the former case, electron transfer to the tropylium ion was shown to initiate the vinyl polymerization, whereas in the latter case, the reduction rate of the p-xylylene dication was roughly determined by the use of a spectrophotometric method. The rate of the electron transfer between the triphenylmethyl cation and radical has also been measured with an ESR technique.²⁷⁾ Furthermore, stable aromatic carbanions such as the cyclooctatetraene dianion^{28, 29)} and the

heptaphenyltropenide anion,²²⁾ organometallic compounds such as ferrocene^{30, 31)} and triphenyltropylium,³²⁾ and some nitrogen-³³⁾ and oxygen-containing³⁴⁾ compounds have been shown to reduce the cations of tropylium,^{22, 29, 30, 32, 33)} pyrylium,²⁸⁾ and triarylmethyl^{30, 31, 34)} systems.

In the reactions described above, the radical which is produced is either stable enough for the direct observation with ESR or otherwise unstable, easily dimerizing or reacting with oxygen to give the peroxide. In addition, there are some reports that the one-electron transfer to the triphenylmethyl cation from anionic reductants, such as potassium t-butoxide,³⁵⁾ ethyllithium,³⁶⁾ and phenylmagnesium bromide,³⁷⁾ results in coupling of the both reagents to afford the products, which, at first sight, appear to have been formed by an ionic combination reaction.

However, the studies cited above³⁸⁾ are mostly qualitative in nature; heretofore, no attempts have been made to estimate quantitatively the chemical reactivity of the stable carbonium ions in the one-electron reduction.

The purpose of the present study lies in the exploration of new chemical methods to assess the "one-electron" reducibility of stable carbonium ions in the liquid phase, the application of thus obtained methods to the carbonium ions with a variety of structure, and the examination of the structure-reactivity relationship in this reaction.

The present thesis composed of ten chapters. The contents of each chapter will be briefly described below.

In Chapter 2 is described the results of an attempt to estimate the reducibility of the tropylium ion and the triphenylmethyl cation from the different reactivity toward various metals and metallic ions with a wide range of oxidation potentials.³⁹⁾

In Chapter 3 is presented an evidence, shown by the use of the radical trapping technique, of the one-electron transfer mechanism in the zinc reduction of the tropylium ion as a representative case for the metal reduction of stable carbonium ions.⁴⁰⁾

Chapter 4 deals with a mechanistic study on the chromous-ion reduction of the tropylium ion in aqueous media.⁴¹⁾ The role of the various added anions is discussed in detail.

Based on the results obtained in Chapter 4, a kinetic study was carried out on the chromous-ion reduction of some of the substituted tropylium ions, as is described in Chapter 5.⁴²⁾ The results are discussed in comparison with other physicochemical properties of the cations, such as electron affinities, polarographic half-wave potentials, and pK_R^+ values, to show the validity of the present method for the estimation of the "one-electron" reducibility of stable carbonium ions.

In Chapter 6, the work is extended to a series of the aryltropylium and n-alkyltropylium ions, in order to examine the substituent effects exerted upon the seven-membered ring acrossed a phenyl group and of the n-alkyl group.⁴³⁾

In Chapter 7 is presented the results of the explora-

tion of another method for the estimation of the reducibility, i.e., the competitive reduction with zinc, applicable to a variety of hetero-atom substituted tropylium ions which are quite unstable in aqueous media.⁴⁴⁾ Some synthetic studies of new substituted-tropylium salts are also included.

In Chapter 8, the kinetic study on the chromous-ion reduction is further extended to a series of phenyl- and/or n-propyl-substituted cyclopropenium ions.⁴⁵⁾ The applicability of this method to the carbonium ion with a structure other than the tropylium system is successfully demonstrated.

Chapter 9 is concerned with an ESR study on the homolytic dissociation equilibrium of 7-triphenylmethyl-1,3,5-cycloheptatriene, a cross-coupled product of the radicals formed by the competitive reduction of the triphenylmethylation and the tropylium ion.⁴⁶⁾

Finally, in Chapter 10 is given the general conclusion obtained though the present study.

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Chapter 2 The Reduction of the Tropylium Ion and the Triphenylmethyl Cation with Metallic Powders and Metallic Ions

Introduction

Although the reactivity scale of carbonium ions in a one-electron reduction in gaseous phase has received much theoretical interest in association with the ionization potential of organic radicals to carbonium ions,¹⁾ relatively little attention has been given to the reducibility scale in solutions. Furthermore, the range of carbonium-ion structures investigated is quite small. Heretofore, the tropylium ion,²⁾ the triarylcyclopropenium ion,³⁾ and the polyarylmethyl cations^{2c, 3, 4)} have been reported to be carbonium ions whose reducibilities in the liquid phase have been determined by a polarographical method^{2, 3)} and by the measurement of the reversible-electrode reduction potentials of the equilibrated solutions of carbonium ions and the corresponding radicals.⁴⁾

Thus, a systematic investigation into the reducibility scale in solution for the carbonium ions with a wide range of structures should be of considerable interest. However, preliminary to a systematic scrutiny into the carbonium-ion structure, the exploration of simple reducing agents with

a wide range of applicability is needed because of the restricted applicability of the electrochemical measurements.²⁻⁴⁾

As for the reducing agents of the carbonium ions, Conant and his collaborators⁵⁾ first demonstrated that the vanadous ion reduces various types of stable polyarylmethyl cations. There have since been employed such reductants as the chromous ion,⁶⁾ zinc,⁷⁾ potassium,⁸⁾ sodium,⁹⁾ ferrocene,¹⁰⁾ tetraphenyl-p-xylene,¹¹⁾ the dinegative ion of cyclooctatetraene,¹²⁾ carbazole,¹³⁾ phenylenediamine,¹³⁾ the triphenylmethyl radical,¹⁴⁾ triphenyltropylium,¹⁵⁾ and others.¹⁶⁾ Among these reducing agents we chose various metals and low-valent metallic ions, with the idea that these reducing agents would show various degrees of reducing power corresponding to their oxidation electrode potentials and oxidation-reduction potentials, and that a spectrum of the percentage yield of the reduction products would reflect the intrinsic reducibility of the carbonium ion concerned. In this chapter will be described the results of the reduction of the tropylium ion and the triphenylmethyl cation with these reductants in aqueous and in acetonitrile solutions. Also some discussion will be made on the applicability of the spectrum of the radical yields as a measure for estimating the reducibility of the respective stable carbonium ions.

Experimental¹⁷⁾

Materials. Tropylium fluoroborate was prepared from tropilidene according to the method of Conrow,¹⁸⁾ that is, by hydride abstraction with phosphorus pentachloride and by the subsequent addition of aqueous fluoroboric acid. Tropilidene was prepared by the reaction of a large excess of benzene with diazomethane in the presence of cuprous bromide as a catalyst, according to the method of Müller and Fricke.¹⁹⁾ Triphenylmethyl fluoroborate was prepared by the reaction of triphenylcarbinol with aqueous fluoroboric acid in propionic anhydride, according to the method of Dauben et al.²⁰⁾ Acetonitrile was refluxed over phosphorus pentoxide and distilled; bp 80.8-81.2°C. For all the inorganic reagents, except silver powder, commercial materials were used as received. Metallic silver was prepared by the reduction of silver nitrate with saccharose, as has been described by Brauer,²¹⁾ while metallic copper employed was the electrolytically-prepared material supplied by the E. Merck Co.

The Reduction of the Tropylium Ion in an Aqueous Solution with Metallic Powders. The results are shown in Table 1; the details of the procedure are illustrated in the following description of a representative run with metallic iron.

The Reduction of the Tropylium Ion in an Aqueous Solution with Iron. In a 50-ml, round-bottomed flask

equipped with a magnetic stirring bar, a thermometer, and a nitrogen inlet and outlet, 0.399 g of tropylium fluoroborate (2.24 mmol) was dissolved in 22.4 ml of 0.1 N aqueous hydrochloric acid to give a clear, colorless solution. To the stirred solution of the tropylium ion there was then added a 1.865-g portion of iron powder (200-250 mesh) (33.4 mg atom) under an atmosphere of nitrogen at 30.8°C. The reaction temperature immediately rose by 1.1°C and remained almost constant for 10 min. The reaction mixture was then filtered and washed with three 5-ml portions of 0.1 N aqueous hydrochloric acid and with five 10-ml portions of ether. The amount of the unchanged tropylium ion in the aqueous layer was estimated from the ultraviolet absorbance of the tropylium ion ($\lambda_{\text{max}}^{0.1\text{N HCl}}$ 219 and 275 m μ); 79.4% of the charged ion. The organic layer was washed once with 40 ml of 5% aqueous sodium carbonate and twice with 40 ml of 10% aqueous sodium chloride, dried over magnesium sulfate, concentrated by distillation, and evaporated in vacuo to give 0.0407 g of bitropyl (0.224 mmol, 20.0% yield), identified by the superimposability of the infrared spectrum on that of the authentic sample.

The Reduction of the Tropylium Ion in an Aqueous Solution with Low-Valent Metallic Ions. The results are shown in Table 2; the details of the procedure are illustrated in the following description of a run which affords a small amount (<1% yield) of the reduction product.

The Reduction of the Tropylium Ion in an Aqueous Solution with Ferrous Chloride. In a 50-ml, round-bottomed flask equipped with a magnetic stirring bar, a thermometer, a rubber serum bottle cap, and a nitrogen inlet and outlet, 0.322 g of tropylium fluoroborate (1.81 mmol) was dissolved in 6.0 ml of 0.1 N aqueous hydrochloric acid and then kept under an atmosphere of nitrogen. The aqueous solution of ferrous chloride was prepared by dissolving 1.067 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (5.37 mmol) in 12.1 ml of 0.1 N aqueous hydrochloric acid. The ferrous chloride solution was added with a syringe through the rubber serum cap to a stirred solution of tropylium fluoroborate. A specific change in neither the color nor reaction temperature was observed. The solution was stirred under nitrogen at 18.0-20.0°C for two hours and then extracted with three 20-ml portions of ether. The amount of the unchanged tropylium ion was determined from the ultraviolet absorbance (vide supra) of the aqueous layer (102% of the charged tropylium ion). The organic layer was washed with a 30-ml portion of 5% aqueous sodium carbonate and with two 50-ml portions of 10% aqueous sodium chloride, and was then dried over magnesium sulfate. The dried etheral solution was concentrated and evaporated in vacuo to give 0.0027 g of a colorless oil, which was shown to be a mixture of bitropyl, benzaldehyde, and other minor components by a study of the infrared spectrum. The t.l.c. analysis of the oily product with the authentic bitropyl indicated that the bitropyl content was ca. 38 wt% of the

oil; 0.0055 mmol, 0.6% yield, based on the charged tropylium ion.

The Reduction of the Tropylium Ion and the Triphenylmethyl Cation in an Acetonitrile Solution with Metallic Powders. The results are shown in Table 3; the reaction of the triphenylmethyl cation are illustrated in the following description of a representative run with metallic iron.

The Reduction of the Triphenylmethyl Cation in an Acetonitrile solution with Iron. In a 50-ml, round-bottomed flask equipped with a magnetic stirrer, a thermometer, and a nitrogen inlet and outlet there was placed a 0.504-g portion of triphenylmethyl fluoroborate (1.53 mmol). In a stream of nitrogen 15.3 ml of acetonitrile was added, and a clear, orange colored solution was obtained by magnetic stirring; the initial concentration of the triphenylmethyl cation was 0.100 N. To the stirred solution there was then added a 1.299-g portion of iron powder (150-250 mesh) (23.3 mg atom) under an atmosphere of nitrogen at 20.5°C. The reaction temperature rose by 4.1°C within two minutes and remained almost constant for the rest of the reaction time. With the increase in temperature, it was observed that a white precipitate appeared and was dispersed throughout the reaction vessel. After the reaction time of 10 min, 10-ml portions of water and ether were added to the reaction mixture with continuous stirring in order to stop the reaction by the hydrolysis of the unchanged cation. The reaction mixture was filtered and washed with three

10-ml portions of ether in a stream of nitrogen. Air was then bubbled into the pale yellow organic layer. A white precipitate was formed with the simultaneous disappearance of the yellow color of the solution. This precipitate was filtered, washed with ether, and dried at 60°C under reduced pressure (5 mmHg) to give 0.272 g of white, powdery crystals, identified as triphenylmethyl peroxide by the superimposability of the infrared spectrum; 0.524 mmol, 68.6% yield. The organic layer of the filtrate was separated, washed with a 80-ml portion of 5% aqueous sodium carbonate and with two 80-ml portions of 10% aqueous sodium chloride, and dried over magnesium sulfate. The dried ethereal solution was concentrated by distillation and evaporated in vacuo to give 0.117 g of white crystals: the crystals were identified as triphenylcarbinol by a study of the infrared spectrum; 0.448 mmol, 29.3% yield.

Results and Discussion

Reduction of the Tropylium Ion in an Aqueous Solution with Metallic Powders. A 0.1 N solution of tropylium fluoroborate in 0.1 N hydrochloric acid²²⁾ was treated with various metallic powders at room temperature for ten minutes. As Doering and Knox^{7a)} found in zinc-dust reduction, most of the metals examined (see Table 1) were found to reduce the tropylium ion to bitropyl readily. As Table

1 shows, magnesium, aluminum, manganese, zinc, iron, cadmium, cobalt, tin, lead, and antimony afforded bitropyl in fairly good yields, whereas the yield of bitropyl was poor in the cases of chromium (1%), nickel (0.4%), copper (0.2%), and mercury (0.03%). In each reduction only the unchanged tropylium ion was identified as an organic compound other than bitropyl, and a good material balance (>94%) was obtained. Since these reductions were carried out under heterogeneous conditions and with metals of various grain sizes, the percentage yields of bitropyl might not exactly reflect the intrinsic reducing powers of these metals. However, an examination of the standard oxidation electrode potentials of these metals reveals that there exists a correlation between the spectra of the values of the bitropyl yield and of the oxidation electrode potentials of these metals; that is, under these reduction conditions the reducibility of the tropylium ion seems to correspond to the values of the oxidation electrode potential between those of mercury and silver, i.e., -0.789 and -0.799 V.

Reduction of the Tropylium Ion in an Aqueous Solution with Low-Valent Metallic Ions. An aqueous 0.1 N hydrochloric acid solution of tropylium fluoroborate (0.1 N) was treated with about three equivalents of various metallic ions at room temperature under an atmosphere of nitrogen. As shown in Table 2, bitropyl was readily obtained as the sole product in the reductions with chromous²³⁾ and titanous ions, whereas it was obtained in poor yields in

TABLE 1. THE REDUCTION OF THE TROPYLIUM ION
IN THE AQUEOUS SOLUTION WITH METALLIC
POWDERS AT 21—31°C^{a)}

Metal (fresh)	Oxidation potential ^{b)} (V)	Bitropyl Yield (%)	Tropylium ion, unchanged ^{c)} (%)
Mg (200—250)	2.37	92	3.2
Al (200—250)	1.66	99	0.0
Mn (>400)	1.18	98	1.8
Zn (>400)	0.763	100	0.0
Cr (200—250)	0.74	1.0	99
Fe (200—250)	0.440	20	79
Cd (>200)	0.403	26	73
Co (>250)	0.277	94	0.0
Ni (>400)	0.250	0.4 ^{d)}	95
Sn (>400)	0.136	100	0.0
Pb (200—250)	0.126	60	41
Sb (200—250)	-0.212	5.4	94
Cu (200—250)	-0.521	0.2 ^{d)}	95
Hg (liq.) ^{c)}	-0.789	0.03 ^{d)}	99
Ag (\geq 200)	-0.799	0.0 ^{d)}	99

a) Except when otherwise noted, all reactions were conducted with about 15 molar equivalents of metallic powder under an atmosphere of nitrogen for ten minutes, aqueous hydrochloric acid (0.1N) being used as the solvent. Initial concentration of tropylium fluoroborate was 0.100N.

b) W. M. Latimer, "Oxidation Potentials," Prentice-Hall (1952).

c) The reaction was carried out for 30 min with 50 molar equivalents of mercury, aqueous nitric acid (0.1N) being used as the solvent.

d) Estimated by t.l.c. analysis.

e) Determined by UV spectrophotometry.

TABLE 2. THE REACTION OF THE TROPYLIUM ION IN THE AQUEOUS SOLUTION WITH METALLIC IONS AT 18—28°C^{a)}

Ion	Oxidation potential ^{b)} (V)	Reaction time (hr)	Bitropyl yield (%)	Benzaldehyde yield (%)	Tropylium ion unchanged ^{c)} (%)
Cr(II) ^{c)}	0.41	0.01	100	0.0	0.0
Ti(III)	-0.1	0.17	18	0.0	84
Sn(II)	-0.15	2	0.2 ^{d)}	0.0	97
Cu(I)	-0.153	2	0.02 ^{d)}	0.0	101
Fe(II)	-0.771	2	0.6 ^{d)}	~0.1	102
Hg(I) ^{d)}	-0.920	2	0.0 ^{d)}	35	0.0
Fe(III)		2	0.0 ^{d)}	9.3	65
Hg(II)		2	0.0 ^{d)}	46	0.0
Ag(I)		2	0.0 ^{d)}	~1	100

- a) Except when otherwise noted, all reactions were conducted with three molar equivalents of metal chloride under an atmosphere of nitrogen, and aqueous hydrochloric acid (0.1N) was used as the solvent. Initial concentration of tropylium fluoroborate was 0.100N.
- b) W. M. Latimer, "Oxidation Potentials," Prentice-Hall (1952).
- c) Chromous sulfate was used.
- d) Mercurous nitrate was used, along with 0.02N nitric acid as the solvent.
- e) Determined by UV spectrophotometry.
- f) Estimated by t.l.c. analysis.

the reduction with stannous, cuprous, and ferrous ions. However, the mercurous ion, which oxidation-reduction potential is the lowest among the ions examined, afforded no detectable amounts of bitropyl, but an oxidation product of the tropylium ion, i.e., benzaldehyde,^{24,25)} in the 35% yield. Furthermore, in this reaction the mercurous ion was reduced to metallic mercury by the tropylium ion. The formation of benzaldehyde due to the oxidation of the tropylium ion was also observed in the reaction with mercuric, ferric, and silver ions in yields of 46, 9.3, and <1% respectively (Table 2). Thus, as in the case of metallic powder reduction under heterogeneous conditions, the correlation between the reducing power of low-valent metallic ions, as measured by the use of the yields of bitropyl, and of the oxidation-reduction potential of these metallic ions seems to be fairly good; in Table 2 it is clearly demonstrated that the tropylium ions in aqueous solution can be reduced by the ions with the higher values of the oxidation-reduction potentials than that of ferrous ion, and that under these reaction conditions the oxidation-reduction potential of the tropylium ion seems to be just between those of ferrous and mercurous ions, i.e., -0.771 and -0.920 V.

Reduction of the Tropylium Ion and the Triphenylmethyl Cation in an Acetonitrile Solution with Metallic Powders. Since it has been demonstrated for the tropylium ion that its reducibility can be estimated by the use of a spectrum of bitropyl yields in the reduction with various metallic

powders, the reducibility of the other carbonium ion was examined by the use of this method. Among the other carbonium ions the triphenylmethyl cation was chosen as a representative carbonium ion, which is stable in an acetonitrile solution. For the purpose of comparison, the tropylium ion was reduced also in an acetonitrile solution. In each reduction the respective carbonium ions were allowed to react with 15 molar equivalents of various metallic powders under exactly the same reaction conditions as those employed in the experiments with the tropylium ion in an aqueous solution.

The spectrum of the yields of the reduction product is shown in Table 3, along with the values for the oxidation-electrode potentials of metals and the half-wave potentials of the respective metallic ions in an acetonitrile solution.

In an acetonitrile solution the triphenylmethyl cation was smoothly reduced by zinc dust to the triphenylmethyl radical, which was identified as triphenylmethyl peroxide and a minor amount of benzophenone after its oxidation by air. Similarly, the tropylium ion in acetonitrile was readily reduced by zinc dust to bitropyl, as was observed in an aqueous solution. Iron powder and copper powder also reduced each carbonium ion with ease. It is of interest to note that the yield of bitropyl in copper reduction increased from 0.2% in an aqueous solution (Table 1) to 100% in acetonitrile (Table 3). This dramatic increase in

TABLE 3. THE REDUCTION OF THE TROPYLIUM ION AND THE TRIPHENYLMETHYL CATION IN THE ACETONITRILE SOLUTION WITH METALLIC POWDERS AT 14—24°C^{a)}

Metal (mesh)	Zn (>400)	Fe (150—250)	Ni (>400)	Sb (200—250)	Cu (>400)	Ag (≥200)
Reduction of tropylium ion:						
Bitropyl, yield (%)	100	48	0.1 ^{c)}	2.3	100	0.0 ^{b,c)}
Tropylium ion, unchanged (%) ^{d)}	0.0	—	94	—	0.0	82
Reduction of triphenylmethyl cation:						
Triphenylmethyl radical, yield (%) ^{e)}	73	69	0.6	1.7	63	43
Triphenylmethyl cation, unchanged (%) ^{f)}	19	29	98	100	27	51
—E _{1/2} in acetonitrile ^{g)} (Hg electrode) (V)	0.70	1.00	0.33	—	0.36	—0.32
Oxidation electrode pot. ^{h)} in acetonitrile (V)	0.74	—	—	—	0.38	—0.23

a) All reactions were conducted with about 15 molar equivalents of metallic powder under an atmosphere of nitrogen for ten minutes. Initial concentrations of tropylium ion and of triphenylmethyl cation were 0.100N.

b) Tropone (15% yield), identified by the superimposability of the IR spectrum, was obtained as a reaction product.

c) Estimated by t.l.c. analysis.

d) Determined by UV spectrophotometry.

e) The sum of the yields of triphenylmethyl peroxide and of benzophenone. The yields of benzophenone were ca. 1% for Zn, ca. 4% for Cu, and ca. 2% for Ag. No benzophenone was produced in the reactions with Fe, Ni and Sb powders.

f) Isolated as triphenylcarbinol.

g) The half-wave potentials of the corresponding metallic ions, measured vs. aqueous SCE; I. M. Kolthoff and J. F. Coetzee, *J. Am. Chem. Soc.*, **79**, 870, 1852 (1957).

h) W. A. Plaeskow, *Zh. Fiz. Khim.*, **22**, 351 (1948).

the yield may be a reflection of an intrinsic increase in the reducing power of copper in acetonitrile, as is shown by the relatively higher values of the oxidation-electrode potential of the metal and the half-wave potential of the ion (Table 3), values which are closely related to the stabilization of the cuprous ion caused by the strong solvation by the acetonitrile molecules (see the references cited in Table 3).

As has been shown in an aqueous solution, nickel and antimony, which have relatively lower oxidation-electrode potentials, were found to have low reducing powers in acetonitrile for each carbonium ion, this being shown in the low yields of the reduction product from each carbonium ion (Table 3).

Silver did not show any reducing power to the tropylium ion under these reaction conditions; this is a result similar to that observed in an aqueous solution (Tables 1 and 3). In contrast to this, the triphenylmethyl cation was easily reduced by silver powder, indicating that this cation is more reducible than the tropylium ion (Table 3).

The ready reducibility of the triphenylmethyl cation observed in these experiments is consistent with the following reactivity sequence of these two cations: (a) the half-wave potentials of the tropylium ion and the triphenylmethyl cation, measured in methylene dichloride by direct-current polarography, are estimated to be -0.45 and -0.135 V respectively,^{2c)} showing the ready reducibi-

lity of the latter cation; (b) the ionization potentials of tropylium and triphenylmethyl radicals in the gaseous phase are determined to be 6.60 and 7.25 eV²⁶⁾ respectively, indicating that the former radical is more easily transformed into the tropylium ion (in other words, the tropylium ion is less reducible). The loss of delocalization energy resulting when the tropylium ion is converted to the tropylium radical is calculated to be -0.45β (from the simple H.M.O. theory),²⁷⁾ whereas between the triphenylmethyl cation and radical there exists no difference in delocalization energy. When we assume that reducibility of the cation is governed by the difference in the electronic stabilization (delocalization) energy between the carbonium ion and the corresponding radical, this result of calculation is also consistent with the ready reducibility of the triphenylmethyl cation.

Summary

The reaction of tropylium fluoroborate in an aqueous solution has been carried out at room temperature with powders of various metals (Mg, Al, Mn, Zn, Cr, Fe, Cd, Co, Ni, Sn, Pb, Sb, Cu, Hg, and Ag) under heterogeneous conditions and with several metallic ions (Cr(II), Ti(III), Sn(II), Cu(I), Fe(II), Fe(III), Hg(I), Hg(II), and Ag(I)) in a homogeneous solution. All these reagents, except

Ag, Fe(III), Hg(I), Hg(II), and Ag(I), reduce with ease the tropylium ion to give the troyl radical, which then rapidly couples to bitroyl; their reducing powers, estimated by comparing the yields of bitroyl under the same reaction conditions, correlate with their oxidation electrode potentials and oxidation-reduction potentials. The ferric ion, the mercurous ion, the mercuric ion, and the silver ion afford no bitroyl, but only an oxidation product of the tropylium ion, i.e., benzaldehyde. Silver powder gives neither a reduction nor an oxidation product under these reaction conditions. The reduction has also been carried out in an acetonitrile solution, and the reducibility of tropylium fluoroborate with powders of Zn, Fe, Ni, Sb, Cu, and Ag has been compared with that of triphenylmethyl fluoroborate under heterogeneous conditions. Both the tropylium ion and the triphenylmethyl cation are smoothly reduced by Zn, Fe, Ni, Sb, and Cu in this solvent. The tropylium ion, however, is not reduced by silver powder, while the triphenylmethyl cation is reduced to the triphenylmethyl radical. This greater reducibility of the latter cation is consistent with what could be anticipated from the data of half-wave potentials, ionization potentials, and H.M.O. calculation reported with respect to these two carbonium ions.

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Chapter 3 Trapping of the Cycloheptatrienyl Radical with 2-Methyl-2-nitrosopropane in the Course of Zinc Reduction of the Tropylium Ion

Introduction

In the preceding chapter was described a systematic study on the reduction of the tropylium ion and the triphenylmethyl cation with metals and metallic ions. The study was based on a fundamental supposition that the reduction of the carbonium ion with these reagents invariably proceeds via the formation of the radical species, i.e., with the one-electron reduction mechanism.

In their report on the zinc reduction of the tropylium ion to give bitropyl, Doering and Knox¹⁾ suggested the initial "one-electron" transfer, resulting in the formation of the tropyl (cycloheptatrienyl) radical, and the subsequent radical coupling. This mechanism certainly seems most reasonable, since the course of this reaction was not altered by the presence of water, thereby precluding a carbanionic mechanism. Ever since, zinc has been employed as the "one-electron" reductant by several investigators.²⁾ However, there has not been given any direct and clear evidence for the generation of the radical species in this type of reaction.

Thus, in order to confirm the validity of this mecha-

nism, the "spin trapping" technique³⁾ by the use of t-nitrosobutane (2-methyl-2-nitrosopropane) was applied to the zinc reduction of the tropylium ion as the representative case for the reaction concerned; the results will be presented in this chapter.

Experimental⁴⁾

Materials. Tropylium fluoroborate and t-nitrosobutane were prepared according to the methods of Conrow⁵⁾ and of Emmons,⁶⁾ respectively. Zinc powder was of a reagent-grade quality. THF was distilled over 2,6-di-t-butyl-p-cresol; bp 66.0-66.2°C.

Zinc Reduction of the Tropylium Ion in the Presence of t-Nitrosobutane. Procedures for a representative run with reaction time of 30 min are described below. To a stirred solution of 0.750 g (4.20 mmol) of tropylium fluoroborate and 2.95 g (33.9 mmol) of t-nitrosobutane in 220 ml of H₂O-THF (7:3 by volume), there was added 1.38 g (21.0 mg-atom) of zinc powder under an atmosphere of nitrogen. After the reaction of 30 min at 31°C in the dark, the excessive zinc powder was filtered off. The filtrate was worked up in the usual way to give 0.667 g of partially solidified red oil, which was then chromatographed over 25 g of silica gel (Nakarai, No. II-A, 100-200 mesh). Elution with n-hexane-benzene (4:1 by volume)

afforded 0.180 g (0.989 mmol) of bitropyl as white crystals with an identical infrared spectrum with the authentic sample; 47.1% yield. The fractions eluted with benzene-ether (3:2 by volume) gave 0.317 g (1.79 mmol) of the nitrone I as white crystals, whose identity was established by the infrared and ultraviolet spectra and mixed mp; 42.6% yield; mp 73.0-74.5°C (Lit.⁷⁾ mp 75-76°C). On the other hand, fractions eluted with ethanol and the ethereal extracts of the aqueous layer which had been made alkaline gave 0.0870 g⁸⁾ (0.978 mmol) of N-t-butylhydroxylamine as pale yellow crystals which exhibited the identical infrared spectrum as the authentic sample; 2.9% yield based on t-nitrosobutane; 23.3% of the tropylium ion used.

In another run with the half scale of the above-mentioned reaction, after the reaction time of 5 min and the usual work-up, the reaction mixture was distilled under vacuum to give 0.0184 g of a brownish-red oil; bp 70-85°C (bath temperature)/0.4 mmHg. The distillate was immediately dissolved in benzene and sealed in a Pyrex tube (outer diameter, 4mm) under vacuum. An ESR spectrum was taken on the sample to give the results described in the text.

Hydrogenation of the Crude Product Mixture. In the same way as described above, 1.00 g (5.60 mmol) of tropylium fluoroborate was reduced with 1.83 g (28.0 mg-atom) of zinc powder in the presence of 3.90 g (44.8 mmol) of t-nitrosobutane in 292 ml of H₂O-THF (7:3 by volume) at room temperature. After 1 min, the reaction mixture was worked up

and concentrated in vacuo to ca. 10 ml, which was subsequently hydrogenated over 0.8 g of palladium carbon (Nakarai, 5%) in dry THF to give 0.519 g of a yellowish oil. From this oil were isolated 0.315 g (1.62 mmol) of bicycloheptyl (58% yield; NMR, τ_{CCl_4} 7.9 (br m, 2H, methine), 8.5 (br s, 24H, methylene); $\nu_{\text{max}}^{\text{CCl}_4}$ 1450 (sh), 1460, 2870, 2940 cm^{-1}) and 0.088 g (0.51 mmol) of N-t-butyl-N-cycloheptylhydroxylamine (9.2% yield, NMR, τ_{CCl_4} 6.3 (br s, 1H, methine), 7.1 (br s, 1H, OH), 8.5 (br s, 21H, methylene, methyl); $\nu_{\text{max}}^{\text{CCl}_4}$ 1025, 1120, 1215, 1350, 1380, 1450(sh), 1460, 2870, 2930, 3420, 3630 cm^{-1}), by the use of preparative thin layer chromatography over silica gel (Merck, Kieselgel PF₂₅₄) with benzene-ether (2:1) as the eluent.

Found: C, 71.53; H, 12.30%. Calcd for $\text{C}_{11}\text{H}_{23}\text{NO}$: C, 71.30; H, 12.51%.

Reaction of t-Nitrosobutane with Zinc in an Acidic Solution.—ESR Measurement. Into a Pyrex tube (outer diameter, 10 mm) with a capillary side tube (outer diameter 1 mm) for ESR measurement, there was charged 0.020 g (0.23 mmol) of t-nitrosobutane and 0.10 g (1.5 mg-atom) of zinc powder. The tube was connected to a vacuum line and 1.6 ml of a solution of acetic acid (0.04 M) in H_2O -THF (1:1 by volume) was transferred into the tube with vacuum distillation. After sealing off the tube under vacuum, the mixture was shaken at room temperature in the dark and an ESR spectrum of the supernatant solution was

immediately recorded to give the results described in the text.

Thermal Dissociation of Bitropyl in the Presence of t-Nitrosobutane.——ESR Measurement. Into a Pyrex tube (outer diameter, 5 mm) for ESR measurement, there was charged 0.015 g (0.17 mmol) of t-nitrosobutane and 0.090 g (0.50 mmol) of bitropyl, which had been purified by sublimation (51°C/1 mmHg). The tube was connected to a vacuum line and 0.5 ml of dry m-xylene was added by vacuum distillation. After being sealed off under vacuum, the tube was shaken well in the dark and introduced into the ESR cavity, which had been kept at 60°C with a JEOL variable-temperature equipment, JES-UCT-2X. After 10 min, signals composed of an equivalent triplet of doublet ($a_N=14.5$ G, $a_H=2.2$ G) began to appear in the ESR spectrum and kept increasing in intensity.

Results and Discussion

The tropylium ion was allowed to react with an excess of zinc powder in the presence of 8 molar equivalents of t-nitrosobutane in H₂O-THF (7:3 by volume) at room temperature for 30 min. The reaction products were separated by elution chromatography to give bitropyl, α -phenyl-N-t-butyl-nitrone (I), and a comparable amount of N-t-butylhydroxylamine. The product distributions in the shorter

reaction times were also examined to give the results summarized in Table 1.

The yields of bitropyl are almost invariable (50±5%), whereas those of the nitrone I and N-t-butylhydroxylamine

Table 1. The product distribution for the zinc reduction of the tropylium ion in the presence of t-nitrosobutane.^{a)}

Reaction time min	Temp. °C	Yield, %		
		Bitropyl	Nitrone I	Hydroxylamine ^{b)}
1	24.0	50.4	4.4	~ 0
2	31.0	54.3	8.6	~ 0
15	31.0	45.5	32.0	~10.7
30	31.0	47.1	42.6	~21.0

a) [Tropylium fluoroborate] = 1.91×10^{-2} M; [Zn] = 5.0 atom equivalent with respect to the tropylium ion; [t-BuNO] = 0.153 M; Solvent = H₂O-THF (7:3 by volume).

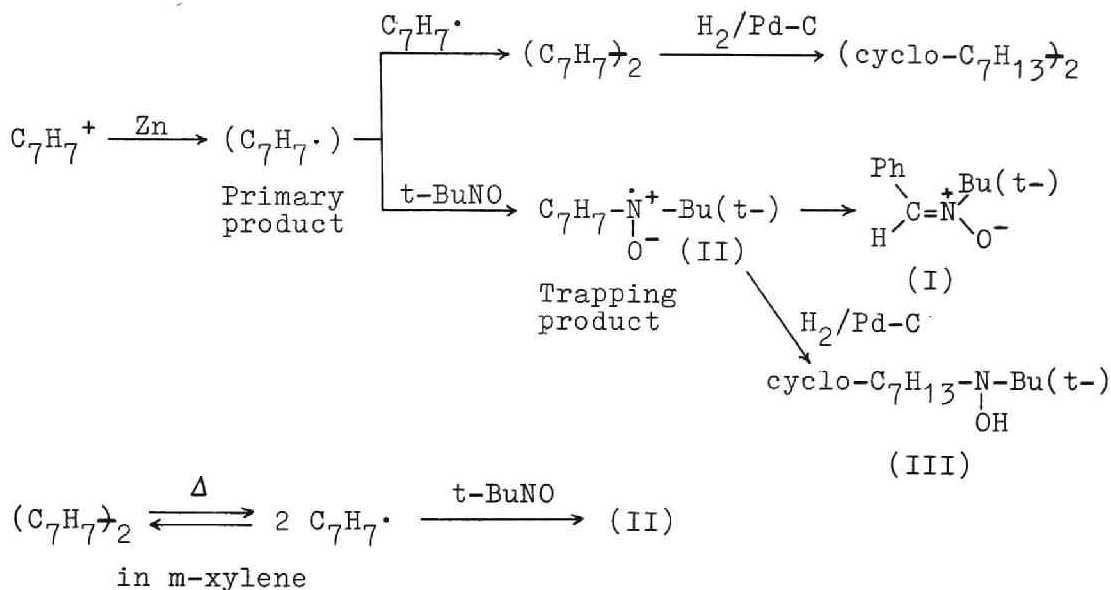
b) N-t-Butylhydroxylamine; the yield is calculated with reference to the tropylium ion. The real yield of this compound is supposed to be greater; see Ref. 8 in the Experimental.

definitely increase with the prolonged reaction time. On the other hand, an analysis with ultraviolet spectroscopy of the aqueous layer revealed that the tropylium ion was completely consumed within one minute.

These results seem to indicate that the zinc reduction, which initially gives a primary product (presumably the troyl radical), is rapidly completed and that about a half of the primary product so formed is trapped by t-nitrosobutane to give a transient product (II), which subsequently rearranges to the nitrone I⁹⁾ (see Scheme 1).

The isolation of this transient product was unsuccessful owing to its instability and volatility. However, the reaction mixture with a short reaction time (5 min), after the usual work-up and vacuum distillation, gave red oil which, after immediate dissolution in benzene, exhibited an ESR spectrum composed of an equivalent triplet of doublet; this radical was assigned to be t-butyl troyl nitroxide (II) ($a_N=14.6$ G, $a_H=2.2$ G), the trapping product. The identical ESR spectrum was observed in the reaction of t-nitrosobutane with the troyl radical, which is produced by the thermal dissociation of bitroyl¹⁰⁾ in m-xylene at 60°C (see Experimental). Furthermore, when the product mixture of a short reaction time (1 min) was catalytically hydrogenated on palladium-carbon, N-t-butyl-N-cycloheptylhydroxylamine (III), which is supposed to be derived from the trapping product (the nitroxide II), was isolated (9% yield) along with bicycloheptyl, which was produced by the

hydrogenation of bitropyl. These results are illustrated in Scheme 1.



Scheme 1

The control experiments to examine the course of the formation of I indicated that the coexistence of three components, i.e., t-nitrosobutane, zinc, and proton,¹¹⁾ is a necessary condition in order to transform II into I. Namely, the three reactions were continued for 30 min, respectively after the immediate removal of t-nitrosobutane (by bubbling off with air), zinc powder (by filtration), and proton¹¹⁾ (by neutralization with NaOH) from the reaction mixtures of a short reaction time (1 min); no more than a trace amount of the nitrone I was detected in the

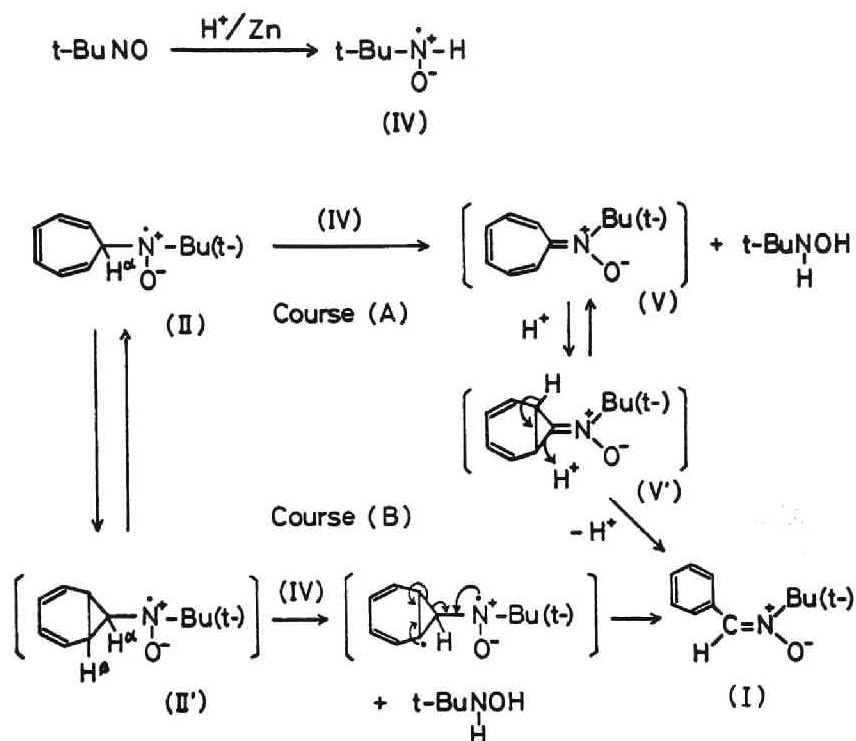
respective reaction mixtures, whereas bitropyl was always found as the major product.

In another control experiment, the interaction of t-nitrosobutane with zinc in aqueous THF solution, acidified by the addition of acetic acid,¹¹⁾ was found to give t-butyl nitroxide (IV), which was identified by the ESR spectrum (an equivalent triplet of doublet; $a_N=13.9$ G, $a_H=12.9$ G¹²⁾). In addition, a nitroxide radical is known to be able to abstract a hydrogen atom.¹³⁾

Consequently, it is most probable that in the mixture of a prolonged reaction time the nitroxide IV is produced in situ, and immediately abstracts a hydrogen atom from the nitroxide II or its valence tautomer II' to give N-t-butylhydroxylamine. This is illustrated in Scheme 2.

In Course (A), the nitron V would be produced by the abstraction of α -hydrogen of the nitroxide II, and subsequently be converted to the nitron I through a norcaradiene-type intermediate V' under the acidic condition in the reaction mixture or in the course of isolation, e.g., during elution chromatography on silica gel.

As for Course (B), it is supposed that the cycloheptatriene-norcaradiene equilibrium lies to the norcaradiene side (II'), when the electron-withdrawing nature of the partially polarized N-O bond in the nitroxide II is taken into consideration.¹⁴⁾ The subsequent β -hydrogen abstraction from the norcaradienyl system (II') to give the benzal system (I) may be plausible from the analogy of the



Scheme 2

ionic rearrangements of the similar type found in literatures.^{1, 15)} Thus, the preferred course (A or B) of the formation of the nitron I from the nitroxide II has not been completely clarified.

However, on the basis of the ESR spectrum of the nitroxide II and of the isolation of the nitron I and also hydroxylamine III from the reaction mixture, it is concluded that the primary product of the zinc reduction of the tropylium ion must be the troyl radical.

Summary

The zinc reduction of the tropylium ion was carried out in the presence of 2-methyl-2-nitrosopropane (a radical scavenger) in H₂O-THF (7:3 by volume) at room temperature. In the reaction mixture with a short reaction time (5 min), t-butyl troyl nitroxide (II) (a radical trapping product) was identified by the ESR analysis. α -Phenyl-N-t-butylnitron (I), which was isolated from the reaction mixture of a prolonged reaction time (30 min), was proved to be derived from the nitroxide II through the hydrogen abstraction by t-butyl nitroxide, which was formed from 2-methyl-2-nitrosopropane in situ in the acidic reaction mixture in the presence of zinc powder. Hydrogenation (on Pd/C) of the product mixture with a short reaction time (1 min) gave N-t-butyl-N-cycloheptylhydroxylamine and bicycloheptyl. On the basis of these observations it is concluded that the primary product of the zinc reduction of the tropylium ion must be the troyl radical.

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- 4) The melting point and boiling point are uncorrected.
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- 7) W. D. Emmons, *ibid.*, 79, 5739 (1957).
- 8) The observed yield of N-t-butylhydroxylamine may be somewhat lower than the real value owing to the experimental loss caused by the high volatility of this compound.
- 9) A control experiment indicated that the tropylium ion itself reacts slowly with t-nitrosobutane to yield a small amount (1.6%) of the nitron I after 30 min at room temperature. However, 68.5% of the tropylium ion was recovered unchanged in this case. An ionic mechanism is supposed to be operating.
- 10) Bitropyl is reported to yield the tropyl radical by the homolytic thermal dissociation (G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, J. Amer. Chem. Soc., 91, 2823 (1969)). Thus, it is most probable that the tropyl radical is trapped by t-nitrosobutane to give t-butyl tropyl nitroxide (II).
- 11) The acidity of an aqueous solution of the tropylium ion

- is reported to be almost equal to that of an aqueous solution of acetic acid (W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 76, 3203 (1954)).
- 12) The lit. ESR: $a_N=13.4$ G, $a_H=12.5$ G (in methanol); $a_N=13.8$ G, $a_H=13.8$ G (in water); the ratio of a_N to a_H is strongly dependent on the solvent polarity (Th. A. J. W. Wajer, A. Mackor, and Th. J. de Boer, Tetrahedron, 25, 175 (1969)).
- 13) For the examples of such a hydrogen abstraction by the nitroxide radical, see a) R. Dupeyre and A. Rassat, J. Amer. Chem. Soc., 88, 3180 (1966); b) M. Iwamura and N. Inamoto, Bull. Chem. Soc. Japan, 40, 703 (1967); c) K. Murayama and T. Yoshioka, *ibid.*, 42, 2307 (1969).
- 14) R. Hoffmann, Tetrahedron Lett., 1970, 2907; and the references cited therein.
- 15) D. Bryce-Smith and W. A. Perkins, J. Chem. Soc., 1962, 5295; b) A. G. Anderson Jr., and L. L. Repologle, J. Org. Chem., 28, 262 (1963); c) P. Beresford, A. Ledwith, and H. J. Woods, J. Chem. Soc. (B), 1970, 257.

Chapter 4 A Kinetic Study on the Reduction of the Tropylium Ion with Cr(II) — The Effect of the Added Anions

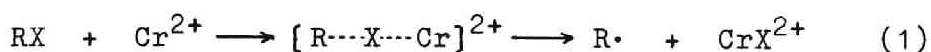
Introduction

In Chapter 2, it was demonstrated that the variation of the reduction-product yields of the stable carbonium ions, observed in the reduction with a series of metals and metallic ions, can be used for a qualitative estimation of the reducibility of the carbonium ions. A mechanistic support for this method was given in a study described in Chapter 3. As an extension of this work, a more quantitative investigation of the reducibility by the use of kinetic measurements seems to be of interest. Among the various reductants examined in the previous work, Cr(II) was found to be a satisfactory reagent, especially for kinetic measurements. This is because the one-electron reduction with Cr(II) proceeds quite readily without forming any by-product, as has already been reported in the case of some carbonium ions.^{1, 2)} Prior to the kinetic study with respect to the reducibility of various stable carbonium ions, it seems necessary to clarify the mechanistic characteristics of this reaction by the use of a single representative carbonium ion, e.g., the tropylium

ion.

In the field of inorganic chemistry, the mechanisms for the reduction of several transition-metal complexes with Cr(II) are well established, and are in general classified into "inner-sphere" and "outer-sphere" mechanisms depending upon whether an electron-transfer bridge between the reductant and the oxidant exists or not.³⁾

On the other hand, for organic compounds, Cr(II) is known to be a potent and versatile reducing agent, and has been used in the reduction of carbonium ions,^{1, 2)} organic halides,^{2c, 4)} olefins,⁵⁾ and carbonyl compounds.^{5a)} Among these reactions, the reduction of organic halides was interpreted as proceeding through reaction sequences analogous to the inner-sphere mechanism mentioned above, with the halide ion acting as an electron-transfer bridge between the organic moiety and Cr(II):^{4a-d, g)}



It is currently accepted that the produced radical species is rapidly captured by the second chromous ion to furnish an organochromic complex, which subsequently dimerizes with an unchanged halide or undergoes protonolysis to give a monomeric hydrocarbon.^{2c, 4c, e)} There is also an exceptional case in which the first-formed radical abstracts the hydrogen atom before the formation of the organometallic complex.^{4g)}

In contrast to the reduction of organic halides, the chromous-ion reduction of carbonium ions usually gives rise to only dimers of the corresponding radicals,^{1, 2)} but no kinetic investigation of this reaction has been reported. We chose the tropylium ion as a representative of stable carbonium ions, and successfully measured the reduction rate with Cr(II) in aqueous solution by the use of the flow method; some findings of the effect of various added anions upon the reduction rate were obtained. The Cr(III) species produced under the various conditions were analyzed chemically and spectrophotometrically. From the results obtained by these experiments, we wish to clarify the mechanism and scope of the reaction in this chapter.

Experimental⁶⁾

Materials. Tropylium fluoroborate was prepared from tropilidene according to the method of Conrow.⁷⁾ The aqueous solutions of the chromous ion were prepared by dissolution of chromium metal (99.99%, Nakarai Co., Ltd.) in 2.9 M respective acid solutions under nitrogen after activation in 2.9 M HCl and rinsing with distilled water. The transfer and dilution of the original chromous solution were done by the use of a hypodermic syringe; distilled water or acid solutions of appropriate concentrations had previously been deoxygenated with nitrogen. The aqueous

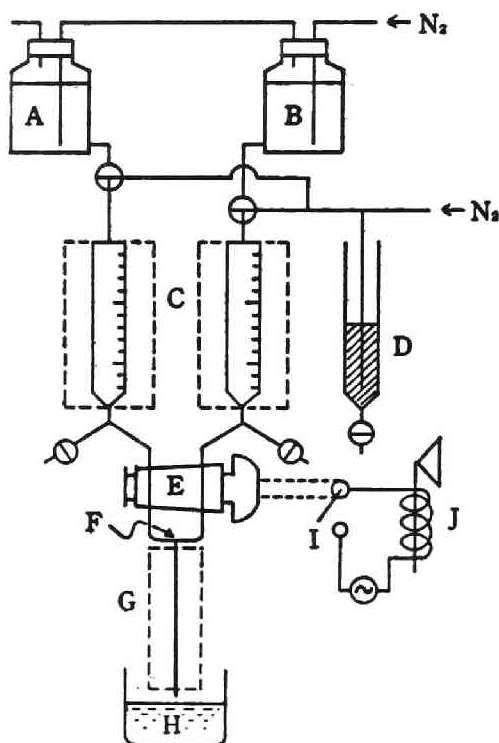


Fig. 1. A schematic diagram of "flow method" apparatus for the kinetic measurements.

A: the tropylium ion, B: Cr(II), C: water-jacketed burette, D: Hg, E: main stopcock, F: mixing chamber, G: water-jacketed reaction tube, H: "stop solution," I: knife switch connected to E, J: buzzer.

solutions of hydrochloric, hydrobromic, sulfuric, perchloric, and fluoroboric acids, the sodium salts of the respective anions, and the sodium bisulfate were of a reagent grade and were used without further purification.

Kinetic Measurements for the Reaction of the Tropylium Ion with Cr(II). The reaction was carried out under a nitrogen atmosphere in the flow system shown in Fig. 1.

Burettes and a reaction tube were covered with jackets circulated with water thermostated at $25.0 \pm 0.2^\circ\text{C}$. The aqueous acid solutions of the tropylium ion and of the chromous ion, the concentrations of which had been determined by ultraviolet spectroscopy and by iodometry, respectively, were charged into each burette from the reservoirs and let stand for at least 10 min for temperature equilibration. The nitrogen pressure in the whole system was raised to 200 mm-Hg above atmospheric pressure, and then the main stopcock was opened for about 4 sec so that 20 ml each of the reagent solutions ran into a glass reaction tube 3.6 mm in inner diameter, through a mixing chamber made of T-shaped glass tube 1.0 mm in inner diameter. The reagents were allowed to react for 0.3-1.5 sec while flowing through reaction tubes of various lengths; then they flowed out into 20 ml of a magnetically-stirred "stop solution" containing 0.5 M CuSO_4 . The operation of the main stopcock was synchronized with a buzzer switch; while the stopcock was opened the buzzer sound was recorded on a tape recorder, and from the distance of the recording tape between the starting and ending points of the buzzer sound the flowing time of the reagents was determined. The time-distance calibration was made by the use of the standard time service of the Nippon Telegram and Telephone Corporation. Thus, when the time required for a total flow of 40 ml was determined to be 4.00 sec, for example, the reaction times were calculated to be 0.26, 0.36, 0.46, 0.60, 0.72, and 1.04 sec with

reaction tubes of the length of 25.1, 35.1, 45.0, 58.8, 70.2, and 102.5 cm respectively. The reaction solution was extracted three times with 50-ml portions of n-hexane, washed with three 100-ml portions of 10% aqueous sodium chloride, and dried over magnesium sulfate. The solvent was evaporated under reduced pressure to give white crystals which were identified as bitropyl from the superimposability of the infrared spectrum with the spectrum of an authentic sample. The amount of the product was determined by ultraviolet spectroscopy in ethanol, using $255\text{ m}\mu$ (ϵ , 7080) as a characteristic band for bitropyl.⁸⁾ The rate constants were determined graphically from the ordinary second-order rate equation. The efficiency of mixing in the mixing chamber was examined by the method described by Roughton,⁹⁾ i.e., the measurement of the heat of neutralization, which was evolved when equivalent aqueous solutions of HCl and NaOH were mixed together under the same conditions as in the chromous-ion reduction. It was confirmed that 100% mixing was attained within 0.02 sec after both reagents flowed through the mixing chamber.

Test for the Efficiency of the Quenching of Cr(II) with Cu(II). To 20 ml of a 2.9 M HCl solution of the tropylum ion (0.02 g-ion/l) and CuSO_4 (0.5 mol/l), was added 10 ml of a 2.9 M HCl solution of Cr(II) (0.04 g-ion/l) under an atmosphere of nitrogen at room temperature. After 10 min, the ultraviolet spectrum of an aliquot showed that the amount of the tropylum ion had not been affected.

The Analysis of Cr(III) Complex in Solution. By the use of an apparatus employed in the kinetic measurements, 40-ml portions each of a solution of the tropylium ion and of Cr(II) in aqueous hydrochloric acid of various concentrations were mixed and allowed to react for 10 min at room temperature under nitrogen in a Erlenmeyer flask, set under the mixing chamber. The initial concentrations of both reagents were set as is shown in Tables 3 and 4 (see Results and Discussion), so that the amount of the tropylium ion was a 1.5-1.8 fold excess. After the extraction of the organic product with three 60-ml portions of n-hexane, the aqueous layer was subjected to the measurement of its visible spectrum or to the chemical analysis of the chloride ion bound to Cr(III) as follows; the free chloride ions in the solution were first determined by conductometric titration with 0.1 M AgNO_3 . The solution was then heated at 100°C for 30 min and titrated again with 0.1 M AgNO_3 . The differences in titers before and after the heating of the solution was regarded as corresponding to the amount of chloride ions bound to Cr(III).

Results

Kinetic Measurements of the Reaction of the Tropylium Ion with Cr(II). As has already been reported,^{1, 2d)} the tropylium ion reacts with Cr(II) quite rapidly and quanti-

tatively to give the dimer, bitropyl. The kinetic measurement of this reaction was made at 25°C by the use of the apparatus depicted in Fig. 1 (see Experimental). The aqueous acid solutions of the tropylium ion and of Cr(II) were mixed in a T-shaped mixing chamber and then allowed to react while flowing down through a reaction tube. The reaction time was 0.2-1.5 sec, depending on the length of the tube. After quenching of the reaction by the use of the instantaneous oxidation of the unchanged Cr(II) with an aqueous solution of CuSO_4 ,¹⁰⁾ bitropyl was extracted with n-hexane and determined by ultraviolet spectroscopy. The initial concentrations of both the reagents were set so that the concentration of Cr(II) would be 1.5 to 3.0 fold greater than that of the tropylium ion. The results for the various reaction times were treated according to the ordinary second-order rate equation (first-order for each reagent) to give a good straight line through the point of origin, as is shown in Fig. 2. The reaction conditions and the graphically-obtained values of the second-order rate constants are listed in Tables 1 and 2.

In a representative run, the unchanged tropylium ion was determined from the ultraviolet spectrum of the aqueous layer, and the material balance was found to be >97.5%. The product, bitropyl, was characterized on the basis of its infrared spectrum, the purity being ascertained by thin-layer chromatography.

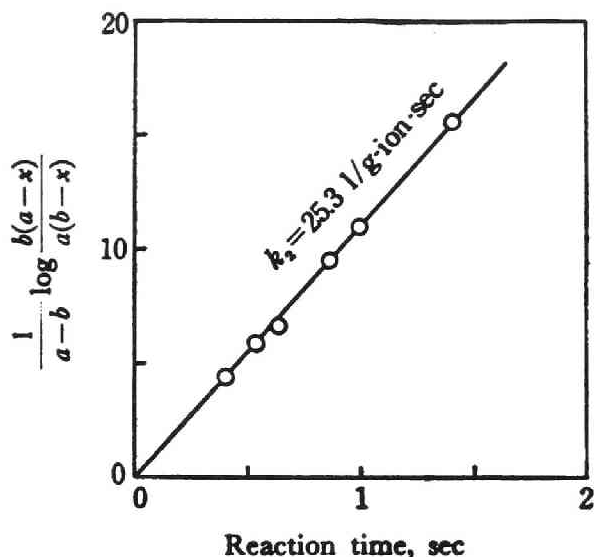


Fig. 2. The rate of the reaction of the tropylium ion with Cr(II) in 0.2 N HCl at 25 °C.
 $[C_7H_7^+]_0 = 0.81 \times 10^{-2}$ g-ion/l
 $[Cr(II)]_0 = 1.8 \times 10^{-2}$ g-ion/l

The Effect of Added Anions on the Reduction Rate.

In order to obtain information on the mechanism operating, especially at the electron-transfer step, the reaction of the tropylium ion with Cr(II) was carried out in aqueous acid solutions containing various anions (Cl^- , Br^- , SO_4^{2-} , HSO_4^- , BF_4^- , and ClO_4^-), which were added as proton acids or as sodium salts; the effects of the concentrations and of the reaction were then examined. Among the results shown in Tables 1 and 2 and in Figs. 3 and 4, the following are noteworthy: (a) Cl^- , Br^- , and SO_4^{2-} have the characteristic effect of increasing the rate of the reaction; (b) this rate-increasing effect approaches its maximum as

TABLE 1. THE RATE CONSTANTS FOR THE REACTION
OF THE TROPYLIUM ION WITH Cr(II) IN AQUEOUS
ACID SOLUTIONS AT 25°C

Solvent		Initial concentration		k_2 l/g-ion·sec
Acid,	N	$C_7H_7^+$ 10 ⁻² g-ion/l	Cr(II) 10 ⁻² g-ion/l	
HCl	0.2	0.81	1.8	25.3
	1.7	0.71	1.6	63.2
	2.9	0.67	1.9	76.6
	2.9	1.8	3.0	74.1
	2.9	2.0	3.7	73.8
	4.4	0.65	1.0	83.0
HBr	0.2	0.85	1.6	24.6
	2.9	0.85	1.1	70.3
	2.9	0.68	1.7	68.0
H ₂ SO ₄	0.05	0.99	3.2	24.9
	0.1	1.0	3.1	27.1
	0.6	1.2	2.1	22.6
	1.0	0.85	2.7	18.8
	1.8	0.81	2.9	14.3
HBF ₄	0.2	2.0	4.0	8.6
	2.9	1.7	27	3.3
HClO ₄	0.2	2.1	5.2	7.6
	1.2	2.4	5.4	4.3
	2.9	1.7	17	1.4

TABLE 2. THE RATE CONSTANTS FOR THE REACTION OF THE TROPYLIUM ION WITH Cr(II) IN THE PRESENCE OF ANIONS ADDED AS SODIUM SALTS IN AQUEOUS ACID SOLUTIONS (0.2 N) AT 25°C

Acid (0.2 N)	Added anion g-ion/l	Initial concentration		k_2 l/g-ion·sec	
		$C_7H_7^+$ 10^{-2} g-ion/l	Cr(II) 10^{-2} g-ion/l		
HCl	Cl ⁻	{ 0.0	0.81	1.8	25.3
		{ 1.0	0.84	2.7	60.2
		{ 2.5	0.56	1.4	84.0
		{ 4.0	0.58	1.0	87.4
HBr	Br ⁻	{ 0.0	0.85	1.6	24.6
		{ 1.0	0.68	2.2	50.6
		{ 1.8	0.93	1.7	65.1
		{ 1.9	0.66	1.4	65.8
		{ 3.4	0.57	1.3	65.8
		{ 4.0	0.93	1.7	65.9
H ₂ SO ₄	SO ₄ ²⁻	{ 0.0	1.0	3.1	27.1
		{ 0.3	0.92	1.9	45.5
		{ 1.0	0.92	2.0	58.0
		{ 1.6	0.82	2.1	64.4
H ₂ SO ₄	HSO ₄ ⁻	{ 0.3	0.90	1.9	33.8
		{ 1.0	0.90	1.8	35.0
		{ 2.0	0.93	1.8	32.9
		{ 3.5	0.88	2.2	26.0
HBF ₄	BF ₄ ⁻	{ 0.0	2.0	4.0	8.6
		{ 1.0	1.9	4.5	6.4
		{ 2.5	2.2	4.4	3.5
		{ 4.5	1.8	5.4	1.4
HClO ₄	ClO ₄ ⁻	{ 0.0	2.1	5.2	7.6
		{ 2.8	2.5	3.5	2.1

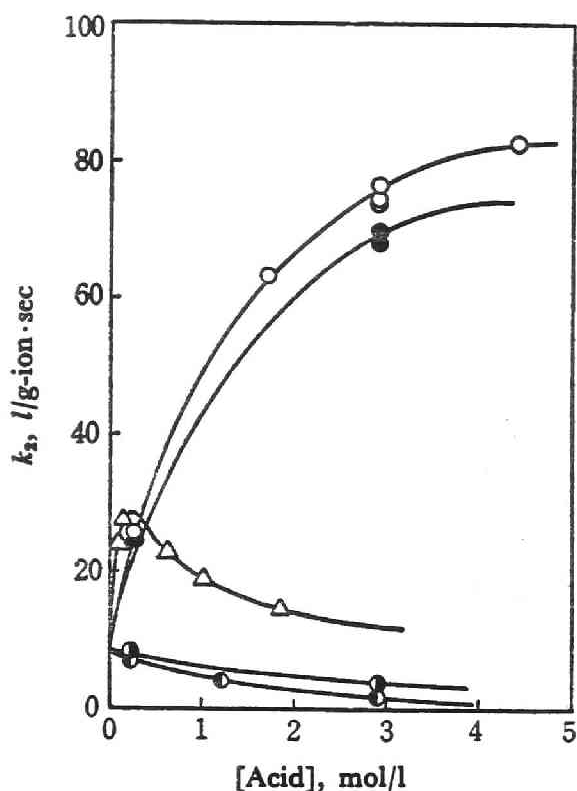


Fig. 3. The effect of anions added as proton acids on the reaction rate.

○: HCl, ●: HBr, △: H₂SO₄, ●: HBF₄, ○: HClO₄.

the concentration of the anion is increased; (c) on the contrary, BF_4^- and ClO_4^- show only a slight rate-retarding effect; (d) the extrapolation of the concentration of each anion leads to the same intercept where $k_2=9$ (1/g-ion·sec) at 25°C; (e) H_2SO_4 and HSO_4^- seemingly exhibit a rate-accelerating effect at lower concentrations and a rate-retarding effect at higher concentrations. Among these findings, the observation (d) clearly indicates that the

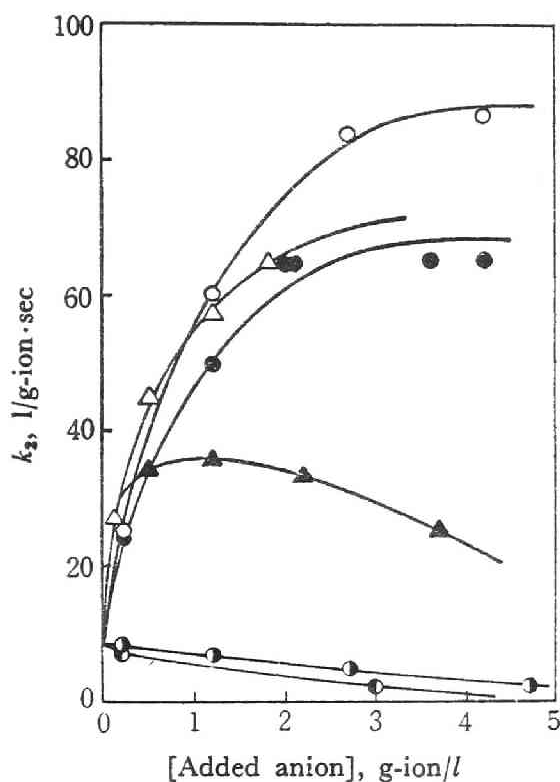


Fig. 4. The effect of anions added as sodium salts on the reaction rate.

○: Cl⁻, ●: Br⁻, △: SO₄²⁻, ▲: HSO₄⁻, ●: BF₄⁻,
●: ClO₄⁻.

presence of halide ions is not essential for the reduction of the tropylium ion, as has been reported in the cases of the triphenylmethyl and diphenylmethyl cations.^{2c)} This result is in sharp contrast to the observation made by Castro^{4b)} that the 1,1-diphenylethyl cation can not be reduced by Cr(II) unless the chloride ion is added. The characteristic effect shown by H₂SO₄ and HSO₄⁻ as described in (e) seems to be attributable to the equilibrium composi-

tion¹¹⁾ of H_2SO_4 , HSO_4^- , and SO_4^{2-} in an aqueous solution; at lower concentrations, the SO_4^{2-} ion, which is predominant as a result of the nearly complete dissociation of H_2SO_4 or HSO_4^- , exerts a rate-accelerating effect, whereas at higher concentrations, undissociated H_2SO_4 and HSO_4^- seem to retard the reaction.

The Analysis of Cr(III) Species. Although Cr(II) is labile to the substitution of its ligands, Cr(III) is known to be sluggish to ligand substitution.¹²⁾ Thus, the analysis of the group attached to Cr(III), which is produced as a result of Cr(II) reduction, makes it possible to deduce the nature of the activated complexes. Taking advantage of these properties, Taube and his coworkers¹³⁾ successfully demonstrated that one-electron transfer reactions from Cr(II) to several inorganic metallic complexes proceed through an activated complex in which a single anion or a molecule acts as an electron-transfer bridge. With the expectation of obtaining information on the function of the added chloride ion on the electron-transfer step, we conducted the reaction of Cr(II) with an excess of the tropylium ion in variable HCl concentrations at room temperature and analyzed the Cr(III) species chemically and by their visible spectra.

An excess of the tropylium ion was allowed to react with Cr(II) in 0.1 to 2.9 M aqueous HCl for 10 min (more than 100 half-lives) under nitrogen; after the subsequent extraction of the organic product, the visible spectrum of

Cr(III) was taken. As is shown in Table 3 and Fig. 5, the absorption maximum of Cr(III) at longer wavelengths was found to make a bathochromic shift to 605 m μ , which cor-

TABLE 3. THE EFFECT OF THE HCl CONCENTRATION ON THE VISIBLE SPECTRA OF Cr(III) FORMED BY THE REACTION OF THE TROPYLIUM ION WITH Cr(II)

Initial concentration			λ_{\max} for Cr(III) m μ
[HCl] N	[C ₇ H ₇ ⁺] g-ion/l	[Cr(II)] g-ion/l	
0.07	0.026	0.014	588
0.14	0.080	0.051	592
0.26	0.080	0.050	595
0.40	0.080	0.050	598
0.55	0.080	0.047	602
0.58	0.080	0.048	602
2.90	0.047	0.029	606

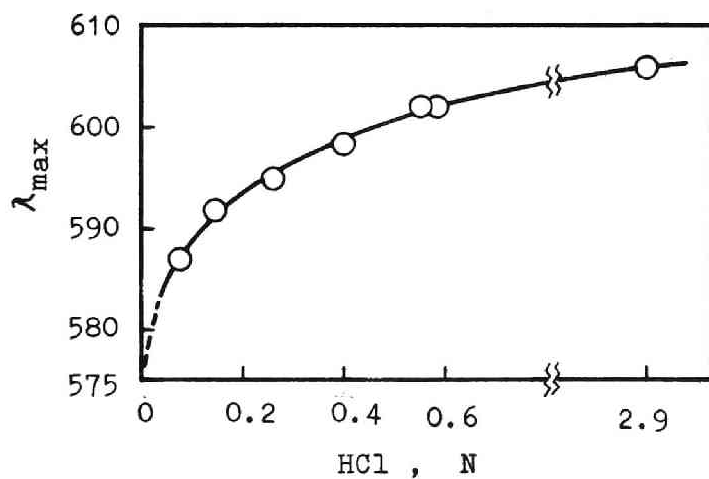


Fig. 5. The effect of HCl concentration on λ_{\max} of Cr(III)

responds to $\text{CrCl}(\text{H}_2\text{O})_5^{2+}$,¹⁴⁾ with an increase in the concentration of HCl. This indicates that the Cr(III) species formed at lower HCl concentration is a mixture of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ ($\lambda_{\text{max}} 575\text{m}\mu$ ¹⁴⁾) and $\text{CrCl}(\text{H}_2\text{O})_5^{2+}$, but at higher HCl concentrations most of the Cr(III) exists as $\text{CrCl}(\text{H}_2\text{O})_5^{2+}$. The results of the chemical analysis of the chloride ion attached to Cr(III) exhibit qualitatively the same tendency, as is shown in Table 4.

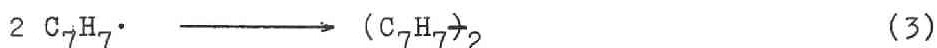
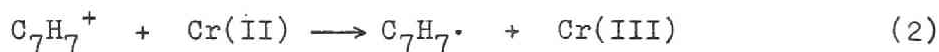
TABLE 4. THE EFFECT OF THE HCl CONCENTRATION ON THE AMOUNT OF THE CHLORIDE ION BOUND TO Cr(III)^{a)}

$\frac{[\text{HCl}]}{N}$	Ratio of Cl bound to Cr(III) to total Cr(III)
0.072	0.47
0.110	0.51
0.139	0.53
0.175	0.59

a) $[\text{Cr(II)}]: 0.014 \text{ g-ion/l}$, $[\text{C}_7\text{H}_7^+]: 0.025 \text{ g-ion/l}$.

Discussion

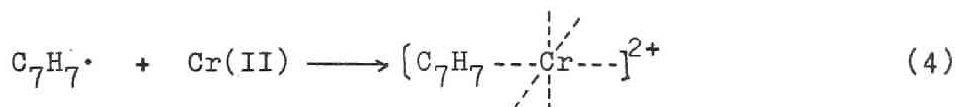
One of the simplest mechanisms for the formation of bitropyyl by the reduction of the tropylium ion with Cr(II) is the radical mechanism shown below:



At present, it still remains open whether the radical produced is entirely free or is loosely affiliated with the metal ion (Step (4)); consequently, the possibilities for

the reactions through $[\text{C}_7\text{H}_7\text{---}\overset{\text{---}}{\underset{\text{---}}{\text{Cr}}}\text{---}]^{2+}$, depicted in Steps

(4) and (5) or in Steps (4) and (6), can not be rigorously eliminated:



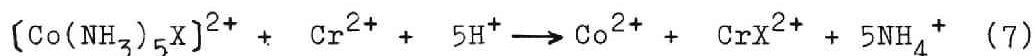
Among these, however, Steps (2) and (3) seem most likely because, regardless of the acidity of the solvent, the

reduction only gives the dimer, and no protonolysis product

(tropilidene) which can be derived from $[C_7H_7 \overset{\cdot\cdot}{\overset{\cdot\cdot}{\text{---}}} \text{Cr} \overset{\cdot\cdot}{\overset{\cdot\cdot}{\text{---}}}]^{2+}$

is ever formed. Furthermore, the marked effect of the added anions on the reaction rate indicates that, in any case, the rate-determining step is Step (2), at which an anion can substantially participate.

A representative example of such an anion-affected reaction may be seen in the reduction of $[Co(NH_3)_5X]^{2+}$ with Cr^{2+} . In this case the transition state in which the anion, X, acts as an electron-transfer bridge has been proposed:¹³⁾

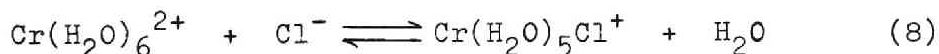


Also, in the present study, the fact that only such anions as Cl^- , Br^- , and SO_4^{2-} , which can coordinate with Cr(III), show the rate-accelerating effect would imply that these anions act as electron-transfer bridges between the tropylium ion and Cr(II). On the other hand, when the anion concentration is graphically extrapolated to zero, the rate constant still has the value of 9 (l/g-ion·sec), indicating that the electron transfer also takes place via the H_2O molecule as a bridge. Thus, in the reaction system, paths which proceed via an anion bridge and those which proceed via an H_2O bridge are both present; they give rise

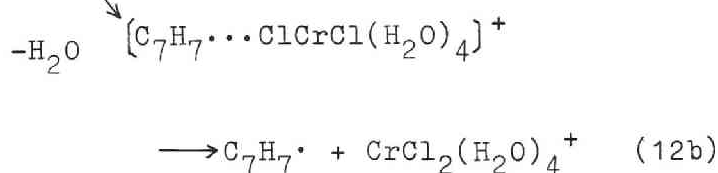
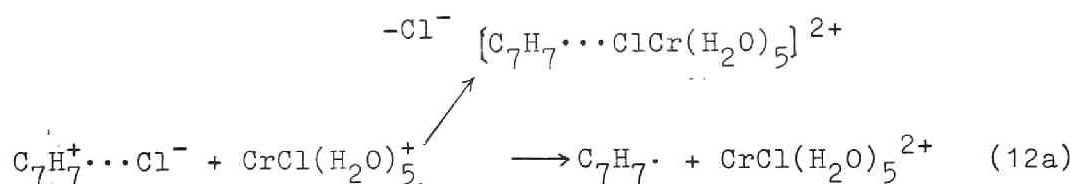
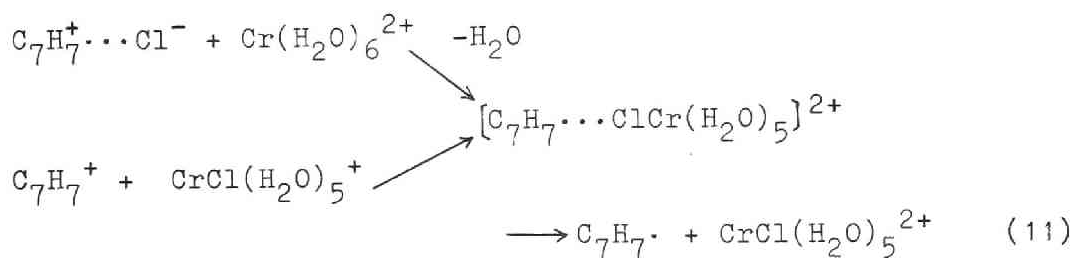
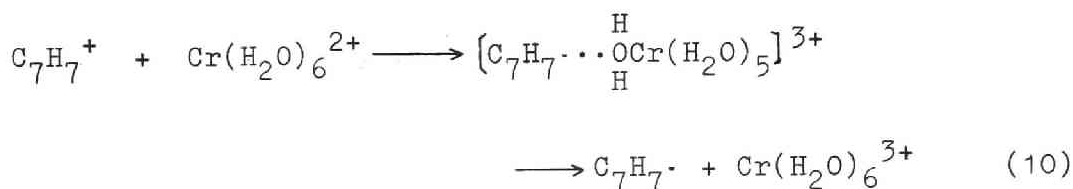
to $\text{Cr}(\text{H}_2\text{O})_5\text{X}^{2+}$ and $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ respectively.

The effect of the added chloride ion on the reaction rate, however, is at most a factor of about 10 (see Fig. 4), much smaller than the factor of 10^6 found in the reaction (7) for the Cl bridging relative to the H_2O bridging.¹⁵⁾ This may indicate that, although there is bridging by the chloride ion between C_7H_7^+ and $\text{Cr}(\text{II})$, it is much less effective than in the case of the reduction of $[\text{Co}(\text{NH}_3)_5\text{X}]^{2+}$ since even in the activated complex, the interaction between C_7H_7^+ and Cl^- is considered to be quite weak because of the complete delocalization of the positive charge in the tropylium ion.

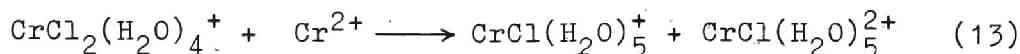
When the reaction is conducted in the presence of HCl , the reacting species which give rise to the chloride-ion bridge is supposed to be $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^+$ ¹⁶⁾ or the ion pair, $\text{C}_7\text{H}_7^+ \cdots \text{Cl}^-$,¹⁷⁾ which is in equilibrium with $\text{Cr}(\text{H}_2\text{O})_6^{2+}$ or with C_7H_7^+ respectively:



Therefore, it may be supposed that, among these species, the following reaction paths (Steps (10)-(12)) are competing with each other:



Path (10) proceeds by means of bridging with H_2O , while Paths (11) and (12) make use of the chloride bridge. As for Path (12), it can not be determined from the analysis of $\text{Cr}(\text{III})$ which course, (12a) or (12b), is pertinent, since $\text{CrCl}_2(\text{H}_2\text{O})_4^+$ is known to react readily ($k_2 \sim 10^2$ l/g-ion·sec at 2°C^{12}) with Cr^{2+} to give $\text{CrCl}(\text{H}_2\text{O})_5^{2+}$, as is shown below:



The tendency of the rate-increasing effect of anions to approach its maximum with an increase in the anion concentration (shown in Figs. 3 and 4) can be ascribed to the shift of the equilibria (8) and (9) to the right, with the result that the reaction proceeds completely via the bridging with the chloride ion so that no more rate acceleration becomes observable. This is also consistent with the result, obtained from the chemical analysis, that the amount of the chloride ion attached to Cr(III) increases with an increase in the HCl concentration.

From these results, it is concluded that the one-electron reduction of the tropylium ion with Cr(II) in the aqueous acid of the appropriate concentration does not occur directly between the two reagents, but proceeds by means of the electron-transfer bridge mechanism. Therefore, it may be expected that, so long as the acid solution is used in a concentration sufficient for the bridging, the reactivity of the various stable carbonium ions in this reaction will mainly reflect the inherent electron affinity of the respective carbonium ions and that the effect of the steric factor will be minimized. The investigation on the correlation of such a reactivity with the electron affinity of the various stable carbonium ions will be described in the following chapter.

Summary

The one-electron reduction of tropylium fluoroborate with Cr(II) was carried out in aqueous solution containing various anions (Cl^- , Br^- , SO_4^{2-} , HSO_4^- , BF_4^- , and ClO_4^-) which were added as proton acids or as sodium salts, and the reaction rate at 25°C was measured by the use of the flow method. It was found that Cl^- , Br^- , and SO_4^{2-} exhibit the characteristic rate-accelerating effect, whereas BF_4^- and ClO_4^- show a slight rate-retarding effect. From the extrapolation of the anion concentration to zero, it was indicated that this reaction can proceed even in the absence of added anions. From these findings, together with the results of chemical and spectrophotometrical analyses of the Cr(III) species, it was concluded that the reduction of the tropylium ion with Cr(II) proceeds through an electron-transfer step where the anion (Cl^- , Br^- , or SO_4^{2-}) or the water molecule acts as a weakly interacting electron-transfer bridge. This mechanism is essentially analogous to the "inner-sphere mechanism" known in the field of inorganic metal complex chemistry.

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Chapter 5 A Kinetic Study on the Reduction of Some Substituted Tropylium Ions with Cr(II)

Introduction

Although the one-electron reduction of carbonium ions in gaseous phase has raised much theoretical interest in association with the ionization potentials of organic radicals to carbonium ions, the reducibility of stable carbonium ions in solution has received rather little attention; quantitative studies of it have been restricted to electrochemical ones, such as polarography¹⁾ and emf measurements of the cells made of equilibrated solutions of the carbonium ions and the corresponding radicals.²⁾

In the preceding chapter, it was shown that, among various inorganic reducing agents, Cr(II) is a suitable reagent for the kinetic study designed to estimate quantitatively the reducibility of stable carbonium ions in solution.

Thus, the kinetics of the chromous-ion reduction of the substituted tropylium ions were studied with the idea that the change in the electron affinity of these cations caused by the introduction of various substituents will be reflected in the rate of reduction. The relative electron affinities of carbonium ions have been estimated from the

transition energies of the charge-transfer bands, and also from the polarographic half-wave potentials. In this chapter will be discussed the correlation of the reducibility of these carbonium ions with the relative electron affinities thus obtained, and also with the pK_R^+ values measured for the respective cations. Also will be shown the applicability of this method (the chromous-ion reduction) to the evaluation of the reducibility of stable carbonium ions of the tropylium system in solution.

Experimental³⁾

Materials. All the reagents employed were of a reagent-grade quality except when otherwise noted. Acetonitrile and ethyl acetate were refluxed over phosphorus pentoxide and then distilled; acetonitrile, bp 81.0-81.5°C; ethyl acetate, bp 77.0-77.4°C.

Tropylium fluoroborate was prepared from tropilidene according to the method of Conrow.⁴⁾

7-Methyl-, 7-ethyl-, 7-isopropyl-, and 7-*t*-butylcycloheptatrienes were obtained by the reaction of 7-ethoxycycloheptatriene with the corresponding alkylmagnesium halides, as has been reported by Nozoe and his co-workers;⁵⁾ 7-methylcycloheptatriene, bp 53°C/63 mmHg (lit, bp 63°C/80 mmHg⁵⁾); 7-ethylcycloheptatriene, bp 84°C/35 mmHg; 7-isopropylcycloheptatriene, bp 88°C/36 mmHg (lit, bp 74°C/

33 mmHg⁵⁾); 7-t-butylcycloheptatriene, bp 90°C/24 mmHg (lit, bp 95-98°C/45 mm Hg⁵⁾).

7-Phenylcycloheptatriene was prepared by the reaction of tropylium fluoroborate with phenyllithium according to the method of Doering and Knox;⁶⁾ bp 76°C/0.4 mmHg.

7-Triphenylmethylcycloheptatriene was synthesized by reference to the thesis of Rifi.⁷⁾ In a 100-ml four-necked flask equipped with a mechanical stirrer, a thermometer, and a nitrogen inlet and outlet, there was stirred a suspension of 1.467 g (8.74 mmol) of tropylium fluoroborate in 40 ml of dry ethyl ether. To this mixture was slowly added 63 ml of a 0.14 M ethereal solution of triphenylmethylsodium (8.8 mmol), prepared from triphenylmethyl chloride and 1% sodium amalgam according to the method of Renfrow and Hauser,⁸⁾ over a 10-min period by the use of a hypodermic syringe. The dark red color of the solution of triphenylmethylsodium was instantaneously discharged when it was added to the ethereal suspension of tropylium fluoroborate. The yellowish gray mixture was stirred for a further 2 hr at 24-26°C under nitrogen. After the addition of 100 ml of water, the organic layer was separated and worked up in the usual way to give 2.928 g of a yellowish white solid, which was then chromatographed over 100 g of silica gel (Nakarai, No. II-A, 100-200 mesh). Elution with n-hexane-benzene (4:1) gave 1.263 g (3.78 mmol) of 7-triphenylmethylcycloheptatriene as white crystals; the same infrared spectrum as the authentic sample; 43.3% yield; mp 166.6-170.7°C

(dec) (lit, mps 167-170°C (dec)⁹⁾ and 156°C⁷⁾).

The isomerization of 7-substituted cycloheptatrienes to the mixtures of 1-, 2-, and 3-substituted cycloheptatrienes was effected thermally by successive sigmatropic 1-5 hydrogen shifts,¹⁰⁾ so that the steric hindrance at the step of hydride abstraction by the triphenylmethyl cation (vide infra) might be diminished. 7-Methyl-, 7-ethyl-, 7-isopropyl-, 7-t-butyl-, and 7-phenylcycloheptatrienes were sealed in Pyrex ampoules under vacuum ($<10^{-3}$ mmHg), heated in an oil bath at 175°C for 1.5 hr,⁵⁾ and distilled under reduced pressure; methylcycloheptatrienes, bp 65-67°C/72 mmHg; ethylcycloheptatrienes, bp 95-98°C/41 mmHg; isopropylcycloheptatrienes, bp 90-94°C/35 mmHg; t-butylcycloheptatrienes, bp 79-80°C/24 mmHg; phenylcycloheptatrienes, bp 77-79°C/0.4 mmHg. 7-Triphenylmethylcycloheptatriene was dissolved in m-xylene and similarly sealed in a Pyrex ampoule under vacuum. After heating at 145°C for 5 hr, the isomeric mixtures were recovered as white crystals by chromatography over silica gel (Nakarai, No. II-A, 100-200 mesh), with n-hexane-benzene (4:1) as the eluent.

Methyltropylium perchlorate (Ia) was synthesized following the method of Corrow.¹¹⁾ Into a suspension of 7.00 g (0.0204 mol) of triphenylmethyl perchlorate in 40 ml of acetonitrile, we added 2.079 g (0.0195 mol) of thermally-isomerized methylcycloheptatrienes with magnetic stirring at room temperature. In 1 min, the precipitates of triphenylmethyl salt all dissolved. After 10 min,

the solvent was evaporated under reduced pressure, a 50-ml portion of ethyl acetate was added, and the yellow solid mass was pulverized. Then the mixture was evaporated again, followed by the addition of another 100 ml of ethyl acetate and by the trituration of the solid. This time the precipitates were collected under a stream of nitrogen, washed with ten 10-ml portions of ethyl acetate, and dried in a vacuum desiccator to give 3.879 g (0.0190 mol) of crude Ia; 97.4% yield. Recrystallization from acetonitrile-ethyl ether under nitrogen gave white crystals, which rapidly decompose on exposure to air; mp 110.0-111.5°C (lit, mps 111-112°C¹¹) and 109°C¹²); $\lambda_{\text{max}}^{0.1\text{M HCl}}$ 287 m μ (ϵ , 4760) (lit, $\lambda_{\text{max}}^{\text{conc H}_2\text{SO}_4}$ 288 m μ (ϵ , 3500)¹²).

Ethyltropylium perchlorate (Ib) was obtained from the isomerized ethylcycloheptatrienes, as white crystals with a pink tinge, by the same method; 90.5% yield; mp 84.0-84.3°C; $\lambda_{\text{max}}^{0.1\text{M HCl}}$ 292 m μ (ϵ , 4880).

Isopropyltropylium perchlorate (Ic) was similarly prepared as brownish-white crystals from the isomerized isopropylcycloheptatrienes, except that dry ethyl ether was employed instead of ethyl acetate for the washing of the product; 76.7% yield; mp 35.8-39.8°C; $\lambda_{\text{max}}^{0.1\text{M HCl}}$ 294 m μ (ϵ , 5030).

t-Butyltropylium perchlorate (Id) was obtained as white crystals by the same procedure as was used in the preparation of Ia except that the reaction time was prolonged to 2 hr; 64.0% yield; mp 179.0-180.0°C (dec);

$\lambda_{\text{max}}^{0.1\text{M HCl}}$ 293 m μ (ϵ , 4880).

Phenyltropylium fluoroborate (Ie) was prepared as yellow crystals by the same method, except that triphenylmethyl fluoroborate was used instead of perchlorate salt; 74.9% yield; mp 151.0-152.0°C (lit, mp 153-154°C¹³); $\lambda_{\text{max}}^{0.1\text{M HCl}}$ 226 m μ (ϵ , 37700), 270.5 m μ (14800), 368 m μ (16200).

Triphenylmethyltropylium fluoroborate (If) was synthesized by an essentially similar method. In a 100-ml two-necked flask equipped with a thermometer and a reflux condenser connected to soda-lime tube, was charged a solution of 0.330 g (1.00 mmol) of triphenylmethyl fluoroborate in 15 ml of acetonitrile. To this solution was then added 0.336 g (1.04 mmol) of thermally-isomerized triphenylmethylcycloheptatrienes, and the whole mixture refluxed for 6.5 hr. The reaction mixture was then evaporated in vacuo, pulverized in 7 ml of freshly-added ethyl acetate, and evaporated again. Then an 18-ml portion of ethyl acetate was added; the yellowish precipitates were then collected, washed with three 5-ml portions of ethyl ether, and dried under reduced pressure. Recrystallization of the crude product from acetonitrile-ethyl ether yielded 0.204 g (0.485 mmol) of If as white crystals with a silvery tinge; 46.6% yield; mp 243.0-243.5°C (dec); $\lambda_{\text{max}}^{2.9\text{M HCl}}$ 226.5 m μ (ϵ , 46600), 260 m μ (sh) (10500), 309 m μ (5850); NMR, $\tau_{\text{CH}_3\text{CN}}$ 0.44 (m, 6H, tropylium ring protons), 2.34 (s, 15H, phenyl protons).

Found: C, 74.25; H, 4.77%. Calcd for $\text{C}_{26}\text{H}_{21}\text{BF}_4$: C,

74.30; H, 5.04%.

The solution of chromous chloride in 10% HCl (2.9 M) was prepared as has been described in the previous chapter.

One-Electron Reduction of the Substituted Tropylium Ions with Cr(II). In a 100-ml, four-necked flask equipped with a magnetic stirring bar, a serum rubber cap, and a nitrogen inlet and outlet, there was charged a solution of 0.258 g (1.05 mmol) of Id in 40 ml of 10% HCl. To this solution was then added 5 ml of 1 M solution of chromous chloride in 10% HCl (5 mmol) by the use of a hypodermic syringe under an atmosphere of nitrogen. The reaction mixture immediately became cloudy with an organic substance dispersed in the solution. The mixture was stirred for 10 min and worked up in the usual way to give 0.157 g (0.534 mmol) of x,x'-di-t-butylbitropyl as a viscous oil; 100.1% yield; NMR, τ_{CCl_4} 3.3-4.1 (m, 6.2H, H^{3-6}), 4.7-5.1 (m, 3.8H, $\text{H}^{2,7}$), 8.2 (s, 2H, H^1), 8.8, 8.9 (two s, 18H, t-butyl).

Reductions of Ia, b, c, e and f were carried out in the same way. The ultraviolet spectra and the results of the elementary analyses of all the products are tabulated in Table 1.

Kinetic Measurements. The reaction rate was measured in 10% HCl at $25.0 \pm 0.2^\circ\text{C}$ by a method described in the preceding chapter. The products were determined by ultraviolet spectroscopy using the characteristic bands listed in Table 1.

Measurements of the Charge-Transfer Bands with Pyrene. In 5 ml of the solution of pyrene in 1,2-dichloroethane

TABLE 1. ULTRAVIOLET SPECTRAL AND ELEMENTARY ANALYTICAL DATA FOR α,α' -DISUBSTITUTED BITROPYL

Substituent	$\lambda_{\text{max}}^{\text{SOH}}$ m μ (ϵ)	Formula	Elementary analysis			
			Found C%	H%	Calcd C%	H%
Methyl	254 (7400)	$\text{C}_{18}\text{H}_{18}$	91.51	8.75	91.37	8.63
Ethyl	254 (7140)	$\text{C}_{18}\text{H}_{22}$	90.81	9.53	90.69	9.31
Isopropyl	254 (7780)	$\text{C}_{20}\text{H}_{26}$	90.45	9.83	90.16	9.84
<i>t</i> -Butyl	251 (7810)	$\text{C}_{22}\text{H}_{30}$	89.60	10.24	89.73	10.27
Phenyl	239 (37400) ^{a)}	$\text{C}_{26}\text{H}_{22}$	93.27	6.64	93.37	6.63
Trityl	261 (10100)	$\text{C}_{32}\text{H}_{42}$	93.37	6.35	93.65	6.35

a) With a shoulder at 275 m μ (13700).

(0.2 M) was dissolved 2-4 mg of the purified sample of the substituted tropylium ion salt, so that the concentration of the cation became 2×10^{-3} g-ion/l. A red color immediately developed; the visible spectrum was then recorded to give the results shown in Table 4 (see Results & Discussion).

Determination of pK_R 's. The determination of the pK_R in 23% aqueous ethanol was carried out spectrophotometrically following the method of Breslow and Chang.²¹⁾ The ultraviolet spectrum was recorded on each cation in nine or ten solutions of buffer spaced through a pH range of about two units on each side of the pK_R . The buffer solutions were made up from various mixtures of 0.1 M citric acid and 0.2 M Na_2HPO_4 according to the procedure of Gomori.¹⁴⁾ The absorbance at a wavelength characteristic of the cation, described above, was plotted against the pH to give a classical titration curve, whose midpoint was taken as the pK_R . The pH's were read on a Horiba model H pH meter calibrated with standard buffers before use.

Polarography. The polarograms were obtained on the solutions of the respective cations in acetonitrile (1.0×10^{-3} g-ion/l) containing $Et_4N^+ClO_4^-$ (0.5 M) as the supporting electrolyte at 25°C. As the reference electrode, we used the Ag/AgCl electrode described by Popov and Geske,¹⁵⁾ whose potential was found to be -0.162 V vs. SCE.

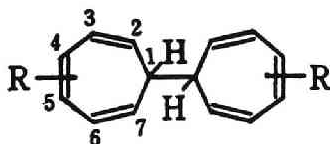
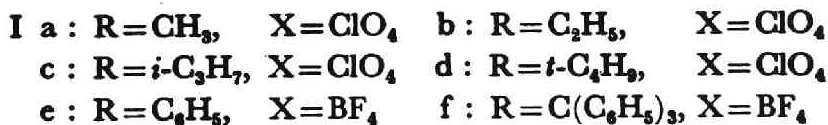
Results and Discussion

Reduction of the Substituted Tropylium Ions with Cr(II).

It has been reported that the tropylium ion was readily reduced with Cr(II) to give a quantitative yield of the dimer, bitropyl.¹⁶⁾ We have ourselves examined the reduction of the substituted tropylium salts (Ia~f) with Cr(II) in 10% HCl (2.9 M);¹⁷⁾



I



II

We ascertained that, in each case, the dimer (II) was obtained in a yield of more than 95% without the formation of any by-product. The elemental analysis of the respective reaction products gave satisfactory values for the dimers. The NMR spectra (60 MHz) of the dimers showed three groups of multiplets, centered at about τ 3.5, 3.9, and 4.8, along with a broad singlet at about 8.0, typical

of a cycloheptatrienyl system, and also the signals corresponding to each substituent. The complex patterns of these multiplets and the multiplicity of the signals of the substituents suggest that the product is a mixture of isomers of α,α' -disubstituted bitropyl (II). The signals centered at τ ca. 3.5 ($H^{4,5}$) and at ca. 3.9 ($H^{3,6}$) were not fully separated; therefore, integration was made for these four protons (H^{3-6}) as one group. It was found that, although the average of from three to five integrations constantly gave the relative ratio of nearly 1:5 for $H^1:H^{2-7}$, the averaged ratio for $H^{2,7}:H^{3-6}$ varied with the substituents, as is shown in Table 2. Though each integration includes the probable error of ca. 5%, there is still a clear tendency for the integrated value of H^{3-6} to decrease

TABLE 2. RATIO OF THE INTEGRATIONS FOR RING PROTONS OF α,α' -DISUBSTITUTED BITROPYL

Substituent	H^1	$H^{2,7}$	H^{3-6}
None	2.0	4.0	8.0
Methyl	$\sim 2^a$	2.94	7.06
Ethyl	$\sim 2^a$	3.36	6.64
Isopropyl	1.90	3.48	6.52
<i>t</i> -Butyl	1.80	3.76	6.24
Phenyl	1.88	4.10	5.90
Trityl	2.00	3.74	6.26

a) Not determined separately because of the substituent signals which appear at the same position.

with the increase in the bulkiness of the substituent. This seems to reflect the steric hindrance exerted upon the coupling of the substituted tropyli radicals formed by one-electron transfer. Each product mixture seemingly gave one or hardly separating two spots on a silica-gel thin-layer plate (n-hexane-benzene, 9:1, as the solvent), but all attempts to isolate the single isomer were unsuccessful.

Kinetic Measurements of the Reduction of the Substituted Tropylium Ions. In order to examine the influence of substituents on the reducibility, the rate of the chromous-ion reduction of various substituted tropylium salts (Ia~f) was measured by the use of the flow method previously described; the reaction was carried out at 25°C under a nitrogen atmosphere in 10% HCl for 0.2~1.5 sec; the conversion was determined by the ultraviolet spectroscopy of the dimers. The reaction was found to follow good second-order kinetics with respect to each substituted tropylium ion and Cr(II). The results shown in Table 3 demonstrate that, whereas the reactivity of the tropylium ion is markedly increased by the introduction of phenyl and triphenylmethyl substituents, it is suppressed by the introduction of alkyl groups, among which the effect gradually increases in this order; methyl, ethyl, isopropyl, and t-butyl groups.

In a mechanistic study described in the previous chapter, it was indicated that the reduction of the tropy-

lium ion with Cr(II) in 10% HCl proceeds through a transition state, in which the chloride ion acts as an electron-transfer bridge between the two reactants, rather than by direct interaction between them. Therefore, it was expected

Table 3. Second-order rate constants for the reaction of substituted tropylium Ions with Cr(II) in 10% HCl at 25°C

Substituent	Initial concn		k_2 1/ g-ion·sec	k_2 average 1/ g-ion·sec
	$R-C_7H_6^+$ 10 ⁻² g-ion/l	Cr(II) 10 ⁻² g-ion/l		
None	{ 2.05 1.80 }	{ 3.75 3.05 }	{ 73.8 74.1 }	74.0
Methyl	{ 1.99 2.60 2.61 }	{ 4.12 5.39 5.20 }	{ 11.1 11.0 11.3 }	11.1
Ethyl	{ 2.48 2.50 2.60 }	{ 4.87 5.22 5.22 }	{ 9.90 9.80 11.1 }	10.3
Isopropyl	{ 2.23 2.46 }	{ 5.26 5.31 }	{ 8.18 8.26 }	8.22
<i>t</i> -Butyl	{ 2.07 2.47 2.51 }	{ 4.83 5.06 5.78 }	{ 8.16 7.74 8.05 }	7.98
Phenyl	{ 0.426 0.462 }	{ 0.857 0.928 }	{ 140 147 }	144
Trityl	{ 0.096 0.099 0.103 0.113 0.114 }	{ 0.453 0.288 0.312 0.226 0.253 }	{ 610 511 615 510 590 }	567

that the influence of the steric effect exerted by each substituent would be minimized and that the reactivity would mainly reflect the intrinsic reducibility of the respective carbonium ions. This supposition seems to be verified by the fact that the reduction of the tropylium ion with the bulkiest substituents, the triphenylmethyl group, still proceeds most rapidly. Thus, the results of the kinetic measurements should be interpreted in terms of the difference in the intrinsic reducibility of the respective cations. From the observed results, it also appears that the inductive effect of the substituents controls the reducibility sequence ($t\text{-Bu} < i\text{-Pr} < \text{Et} < \text{Me} < \text{H} < \text{Ph} < \text{Ph}_3\text{C}$) and that the π -conjugative stabilization exerts very little effect in the tropylium system.

Correlation of the Reducibility with the Relative Electron Affinity of the Carbonium Ions. It seems that it would be of interest to compare the observed reducibility of each substituted tropylium ion with the electron affinity determined by the other methods. As one of such methods we made use of the measurement of the charge-transfer bands observed between carbonium ions and an aromatic hydrocarbon.¹⁸⁾ From the interpretation according to the donor-acceptor theory of Mulliken,¹⁹⁾ it can be expected that the frequency of the charge-transfer band, ν_{max} , for a series of similar stable carbonium ions with a given donor molecule would correlate with the electron affinities of these carbonium ions. Actually, Feldman and Winstein^{18e)}

estimated the electron affinities of various organic cations, applying the principle mentioned above. In the present study, it was observed that the dissolution of each substituted tropylium salt in a 1,2-dichloroethane solution of a condensed aromatic hydrocarbon, pyrene, immediately gave a red-colored solution. It exhibits a band in the visible region which is not found in the spectrum of either component and which can be regarded as a charge-transfer band. The results are shown in Table 4, along with the values of $\log k_2$ for the chromous-ion reduction. A plot of $\log k_2$ against ν_{\max} exhibits a linear correlation between them, as is shown in Fig. 1.

As another measure of the electron affinity of the carbonium ions, electrochemical reduction potentials were determined by polarography with the dropping mercury electrode. The polarography of the tropylium ion was reported to include an irreversible reduction step.^{1a-c)} While some effects (solvation energy, etc.) other than electron affinity are regarded as being reflected in the half-wave potentials for such an irreversible step, for a series of similar cations the relative potentials will serve as a measure of readiness to accept an electron. The half-wave potentials measured in acetonitrile are listed in Table 4, while the correlation with $\log k_2$ is shown in Fig. 2. The linear correlation observed in Figs. 1 and 2 clearly demonstrates that the reactivity of carbonium ions toward Cr(II) can be used satisfactorily as a measure of the

TABLE 4. RESULTS OF THE MEASUREMENTS OF CHARGE-TRANSFER BANDS, POLAROGRAPHIC HALF-WAVE POTENTIALS AND pK_R 's OF SUBSTITUTED TROPYLIUM IONS

Substituent	$\log k_2^a)$	CT Band ^{b)}		$E_{1/2}^{c)}$ V <i>vs.</i> SCE	$pK_R^{d)}$
		λ_{\max} m μ	ν_{\max} 10 ⁴ cm ⁻¹		
None	1.87	540 ^{e)}	1.852	-0.126 \pm 0.002	4.3 ^{f)}
Methyl	1.05	513	1.949	-0.187 \pm 0.001	
Ethyl	1.01	512	1.953	-0.195 \pm 0.004	
Isopropyl	0.91	505	1.980	-0.235 \pm 0.002	
<i>t</i> -Butyl	0.90	508 ^{g)}	1.969	-0.215 \pm 0.002	5.0
Phenyl	2.16	543	1.842	-0.090 \pm 0.002	4.1
Trityl	2.75	550 ~560	1.818 ~1.786	-0.069 \pm 0.001	3.6

a) The logarithmic value of the averaged rate constant for the chromous-ion reduction of the respective tropylium ions.

b) Measured in 1,2-dichloroethane with pyrene as a donor.

c) Corrected from the values measured in acetonitrile *vs.* Ag/AgCl, whose potential was found to be -0.162 V *vs.* SCE.

d) Measured spectrophotometrically in 23% aqueous ethanol.

e) Lit., λ_{\max} 535 m μ (Ref. 7d, e).

f) Lit., pK_R 4.7 (measured by potentiometric titration in water; Ref. 15).

g) Lit., λ_{\max} 503 m μ (Ref. 7c).

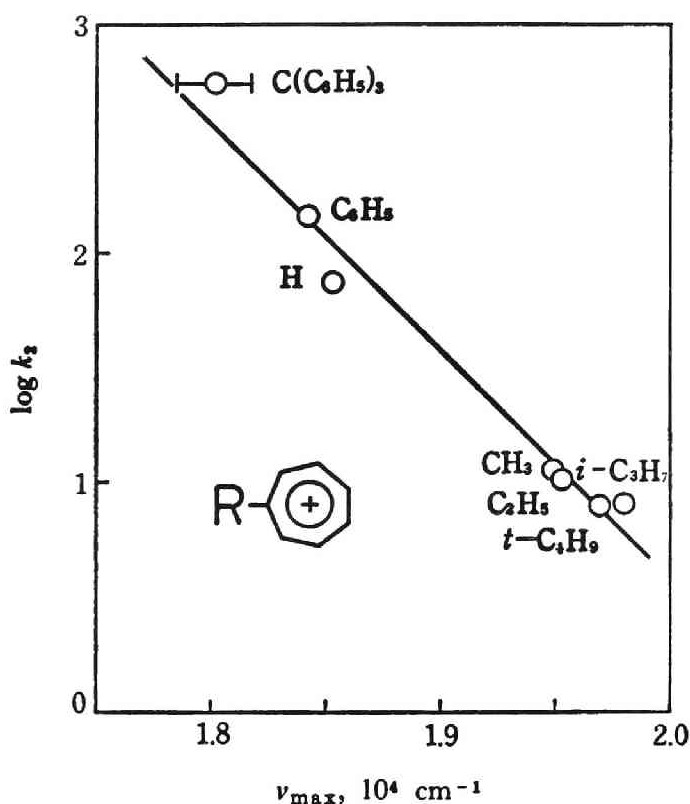


Fig. 1. The correlation of $\log k_2$ with CT transition energies (ν_{\max}).

electron affinity.

Correlation of the Reducibility with pK_{R^+} . In order to examine the correlation between the reducibility and the stability of carbonium ions, the pK_{R^+} values of some representative substituted tropylium ions²⁰⁾ were determined in 23% aqueous ethanol by the spectrophotometric method described by Breslow and Chang.²¹⁾ From the results shown in Table 4, it can be seen that, whereas the alkyl

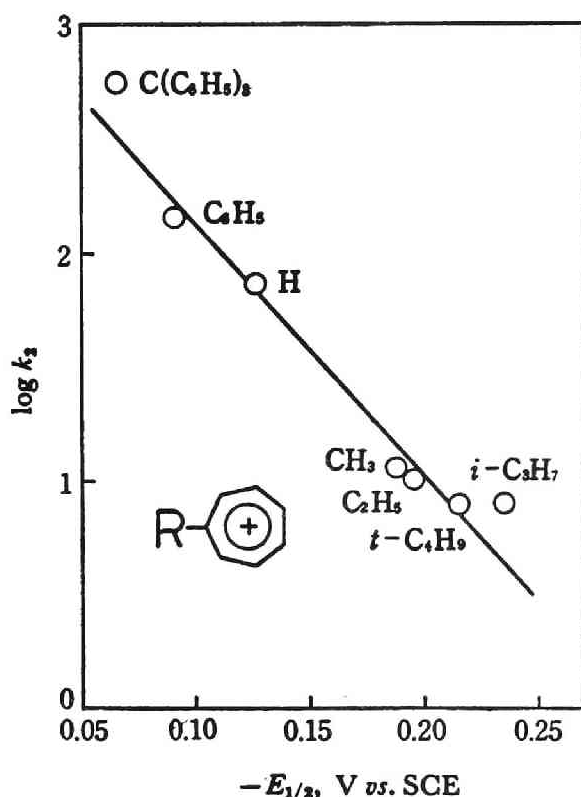


Fig. 2. The correlation of $\log k_2$ with polarographic half-wave potentials ($-E_{1/2}$).

substituent increases the stability, the phenyl group rather destabilizes the cation by means of its electron-withdrawing inductive effect, as is shown by the least stability of the triphenylmethylnitropylium ion. The greater contribution to the stabilization of the cation by the alkyl group than by the phenyl group has been also observed in a cyclopropenyl system.²²⁾

A plot of $\log k_2$ against pK_{R^+} , again, gave a good

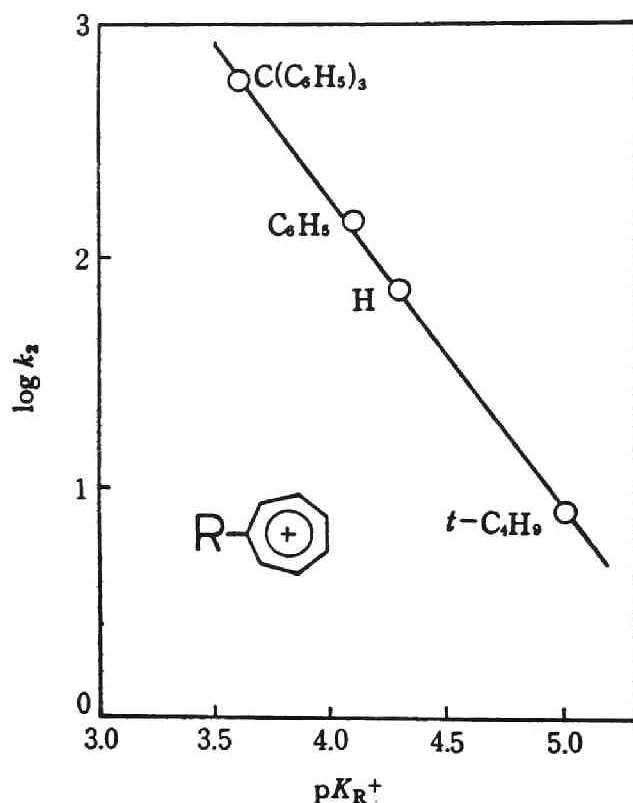


Fig. 3. The correlation of $\log k_2$ with pK_R^+ .

linear correlation, as is shown in Fig. 3. Since the equation for pK_R^+ is written as Eq. (2), with the rate constants for the forward and backward reactions (k_f and k_b respectively), and since it can be assumed that the backward reaction is not greatly affected by the structural change, this correlation may be generalized to imply that the readiness of the carbonium ion to accept one electron is parallel with the reactivity of the ion toward the

electron pair of the nucleophile.



$$pK_{R^+} = \log k_b - \log k_f \quad (2)$$

Summary

The one-electron reduction of the unsubstituted, methyl-, ethyl-, isopropyl-, t-butyl-, triphenylmethyl-, and phenyltropylium ions with Cr(II) in a 10% HCl solution gives, quantitatively, the dimer of the corresponding substituted tropyli radical. The measurements of the reaction rate at 25°C exhibit this order of reactivity: t-butyltropylium ($k_2=7.98$ 1/g·ion·sec), isopropyltropylium (8.22), ethyltropylium (10.3), methyltropylium (11.1), tropylium (74.0), phenyltropylium (144), and triphenylmethyltropylium (567) ions. The values of $\log k_2$ have a linear correlation with the transition energies of the charge-transfer bands observed for these carbonium ions with pyrene, and also with the polarographic half-wave potentials of the respective cations. These correlations indicate that the reactivity of the carbonium ion in the reduction with Cr(II) is determined mainly by the electron affinity inherent in the respective cations. The values of $\log k_2$ also have a good linear correlation with the pK_{R^+} values, implying

a parallelism between the electron affinity and the electrophilicity of these stable carbonium ions.

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Chapter 6 A kinetic Study on the Reduction of the
Aryl- and n-Alkyl-Substituted Tropylium
Ions with Cr(II) — The Effect of the
Substituents

Introduction

In the preceding chapter, it was demonstrated that the reducibility of the substituted tropylium ions determined by the chromous-ion reduction method mainly depends on the electron affinity of respective cations and is also linearly correlated with their pK_R^+ values.

In this chapter are presented the results of a more detailed investigation on the effect of p- and m-substituents on the reducibility of the phenyltropylium ion as studied by the use of the same method. The problem with regard to the nature and extent of the electronic effect exerted by phenyl substituents upon the electronic state of a tropylium ring has aroused much interest among several investigators,^{1, 2)} especially when it is assumed that the plane of the phenyl ring must have a considerable dihedral angle with a seven-membered ring in the phenyltropylium system. Thus, Jutz and Voithenleitner¹⁾ have synthesized a series of aryltropylium ions and discussed on their pK_R^+ 's and electronic spectra; Schuster and his co-workers²⁾

have carried out the HMO calculation on the various aryltropylium ions and compared the results with their electronic and NMR spectra. However, a systematic study on the chemical reactivity of aryltropylium ions seems to have not been reported yet.

In addition, in this chapter will be described the results of some synthetic study on a series of n-alkyltropylium ions and of an examination into the effect of alkyl-chain length upon the properties and reducibility of these cations.

Experimental³⁾

Materials. All the reagents employed were of a reagent-grade quality except when otherwise noted. Acetonitrile and ethyl acetate were refluxed and distilled over phosphorus pentoxide; acetonitrile, bp 81.5-81.7°C; ethyl acetate, bp 77.0-77.4°C. 1,2-Dichloroethane for the measurement of charge-transfer spectra was refluxed and distilled over calcium chloride, bp 83.0-83.5°C.

Aryltropylium ions, Ia-f and Ih, were prepared according to the method of Jutz and Voithenleitner.¹⁾

7-(p-Cyanophenyl)-1,3,5-cycloheptatriene was synthesized from 7-(p-aminophenyl)-1,3,5-cycloheptatriene¹⁾ by reference to the preparation of p-tolunitrile reported by Clarke and Read⁴⁾ as follows. Into 25 ml of 20% HCl was

dissolved 10.0 g (54.6 mmol) of 7-(p-aminophenyl)-1,3,5-cycloheptatriene by vigorous stirring at 60°C for 10 min. To this turbid solution there was slowly added, with ice-cooling, a solution of 3.9 g (57 mmol) of sodium nitrite in 20 ml of water over a 5-min period with magnetic stirring. The mixture was stirred at 0°C for 1.5 hr to give a dark brown solution, which was then neutralized with ca. 7 g of sodium carbonate. On the other hand, 60 ml of the aqueous solution of cuprous cyanide was prepared by the reaction of 8.8 g (180 mmol) of sodium cyanide with the aqueous solution of cuprous chloride, which had been obtained from 17.2 g (68.9 mmol) of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and 4.5 g (77 mmol) of NaCl upon the action of 3.6 g (35 mmol) of NaHSO_3 and 2.4 g (60 mmol) of NaOH in aqueous medium. To a stirred mixture of 50 ml of benzene-ether (4:1) and 60 ml of the aqueous solution of cuprous cyanide, there was added the dark brown solution of the diazonium salt over a 30-min period with ice cooling. The mixture was stirred at 0°C for 40 min, at room temperature for 4 hr, and finally at 60°C for 30 min. The mixture was then extracted with benzene and worked up in the usual way to give 6.1 g of a viscous, dark red oil, which was chromatographed over 130 g of silica gel (Nakarai, No. II-A, 100-200 mesh). From the fractions eluted with benzene was isolated, by the use of preparative thin-layer chromatography over silica gel (Merck, Kieselgel PF₂₅₄) with the same eluent, 1.070 g (5.54 mmol) of crude 7-(p-cyanophenyl)-1,3,5-cyclohepta-

triene, which was then purified by vacuum distillation to give white crystals; 10.1% yield; bp 135°C (bath temperature)/0.05 mmHg; mp 68.5-73.8°C; NMR, τ_{CCl_4} 2.5 (m, 4H, phenyl protons), 3.4 (t, 2H, H^{3,4}), 3.8 (m, 2H, H^{2,5}), 4.8 (d of d, 2H, H^{1,6}), 7.2 (t, 1H, H⁷).

Found: C, 87.13; H, 5.50%. Calcd for C₁₄H₁₁N: C, 87.01; H, 5.74%.

p-Cyanophenyltropylium perchlorate (Ig·ClO₄) was synthesized by the following procedures. To a solution of 0.735 g (3.85 mmol) of 7-(p-cyanophenyl)-1,3,5-cycloheptatriene in 2.4 ml of acetonitrile was added 1.30 g (3.79 mmol) of triphenylmethyl perchlorate. The mixture was stirred at 60°C for 15 min and at 80°C for 3 min to give a dark red solution. Then, 25 ml of ethyl acetate was added and the solution was cooled to 0°C. The glittering crystals which separated out were collected, washed successively with ethyl acetate and dry ether, and dried under reduced pressure to afford 1.021 g (3.50 mmol) of Ig·ClO₄ as yellowish brown crystals; 92.4% yield. The crystals were further recrystallized from acetonitrile-ethyl acetate; mp 212.5-212.8°C (dec); ν^{KBr} 1090 cm⁻¹ (ClO₄⁻), 1480 cm⁻¹ (-C₇H₆⁺), 2240 cm⁻¹ (-CN); $\lambda_{\text{max}}^{10\% \text{ HCl}}$ 228.5 nm (ϵ , 33900), 270.5 nm (18200), 349 nm (17400); NMR, $\tau_{\text{CF}_3\text{COOH}}$ 0.6 (m, 6H, tropylium ring), 1.9 (s, 4H, phenyl).

Found: C, 57.66; H, 3.27%. Calcd for C₁₄H₁₀NClO₄: C, 57.64; H, 3.46%.

7-n-Alkyl-1,3,5-cycloheptatrienes were prepared by the

reaction of 7-ethoxy-1,3,5-cycloheptatriene with n-alkyl-magnesium bromides following the procedures described in the preceding chapter.⁵⁾

Alkyltropylium perchlorates (II, n = 3-6, 8, 12) were synthesized by the hydride abstraction from the corresponding alkylcycloheptatrienes, following the previously-described method.⁵⁾ The melting points and ultraviolet-spectral and analytical data are given in Table 1.

One-Electron Reduction of the Aryl- and n-Alkyl-tropylium Ions. The Chromous-ion Reduction of Ia-h and II (n=3-6). Details of the procedures are illustrated below for the reduction of the p-chlorophenyltropylium ion (Ie) as the representative case. To a magnetically-stirred solution of 0.209 g (0.692 mmol) of p-chlorophenyltropylium perchlorate ($Ie \cdot ClO_4$) in 70 ml of 10% HCl was added 3.5 ml (3.5 mmol) of 1M solution of chromous chloride in 10% HCl by the use of a hypodermic syringe under an atmosphere of nitrogen. The solution was stirred for 5 min at room temperature and then extracted with n-hexane and worked up in the usual way to give 0.140 g (0.347 mmol) of x,x'-di(p-chlorophenyl)bitropyl (x,x'-di-(p-chlorophenyl)biscyclohepta-2,4,6-trien-1-yl) as a partially solidified viscous oil; 100.3% yield; NMR, τ_{CDCl_3} 2.6 (m, 4H, phenyl), 3.1-3.5 (m, 3H, H^{3-6}), 4.4 (m, 2H, $H^{2,7}$), 7.8 (m, 1H, H^1). The chromous-ion reduction of Ia,b,c,d,f,g,h and II (n=3-6) were carried out in the same way to give the dimers in the yield of 100-106%.

Table 1. Physical properties and analytical data of n-alkyltropylium perchlorates

Substituent	mp	UV		Elemental analysis	
		$\lambda_{\text{max}}^{10\% \text{ HCl}}$	(log ϵ)	Found (Calcd)	
	°C	nm		C%	H%
H ^{a)}	>300	273.5	(3.64)	—	—
CH ₃ ^{b)}	110.0- 111.5	287	(3.68)	—	—
C ₂ H ₅ ^{b)}	84.0- 84.3	292	(3.69)	—	—
C ₃ H ₇	36.0- 41.1	296	(3.69)	51.59 (51.62)	5.58 (5.63)
C ₄ H ₉	65.0- 66.3	297.5	(3.78)	53.44 (53.55)	6.10 (6.13)
C ₅ H ₁₁	72.5- 73.9	297.5	(3.77)	55.54 (55.28)	6.58 (6.57)
C ₆ H ₁₃	64.3- 65.2	298.5	(3.75)	56.69 (56.82)	6.85 (6.97)
C ₈ H ₁₇	77.9- 79.5	297.5	(3.76)	59.21 (59.49)	7.64 (7.65)
C ₁₂ H ₂₅	99.0- 100.0	298	(3.75)	63.43 (63.58)	8.75 (8.71)

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b) Data from Chapter 5

The Zinc Reduction of II (n=8,12). To a magnetically-stirred solution of 0.0374 g (0.104 mmol) of n-dodecyltropylium perchlorate in 2.1 ml of acetonitrile, there was added 0.0713 g (1.09 mg-atom) of zinc powder in a stream of nitrogen and the mixture was stirred for 10 min at room temperature. After filtration of the reaction mixture, 5 ml of water was added to the filtrate, which was then extracted with n-hexane and worked up in the usual way to give 0.0303 g (0.0582 mmol) of x,x'-di-n-dodecylbitropyl as a viscous oil; 106% yield; NMR, τ_{CCl_4} 3.4-4.1 (m, 3H, H³⁻⁶), 4.9 (m, 2H, H^{2,7}), 7.9 (br, 3H, H¹ and $\geq\text{C}-\text{CH}_2-$), 8.8 (s, 2OH, $-(\text{CH}_2)_{10}-$), 9.2 (t, 3H, CH₃). The zinc reduction of II (n=8) was conducted in the same way to give the dimer in 95.0% yield.

The Analyses of the Di-Substituted Bitropyls. The elemental analysis and ultraviolet spectroscopy were performed on the reduction products of Ic-h and II (n = 3-6, 8, 12), which were purified by the preparative thin-layer chromatography over silica gel (Merck, Kieselgel PF₂₅₄). The results are listed in Table 2. In the cases of Ia and Ib, the reduction products were not stable enough for the purification with the chromatography. Therefore, they were transformed to x,x'-p-methoxyphenylbiscycloheptyl and analyzed as follows. First, 0.548 g (1.49 mmol) of crude x,x'-di-(p-hydroxyphenyl)bitropyl was catalytically hydrogenated over 1.0 g of palladium carbon (Nakarai, 5%) in 30 ml of dry methanol to give 0.320 g (0.845 mmol) of

Table 2. Spectral and analytical data for x,x'-disubstituted bitropyl

Substituent	UV		Elemental analysis	
	$\lambda_{\text{max}}^{\text{EtOH}}$ nm	(log ϵ)	Found (Calcd) C% H%	
p-HO-C ₆ H ₄ -	243.5	(4.31)	} a)	
	288	(4.16)		
p-CH ₃ O-C ₆ H ₄ -	250 ^{b)}	(4.42)		
	280 ^{b)}	(4.22)		
p-CH ₃ -C ₆ H ₄ -	242	(4.54)	92.78	7.47
	280(sh)	(4.12)	(92.77)	(7.23)
C ₆ H ₅ - ^{c)}	239	(4.57)	93.27	6.64
	280(sh)	(4.10)	(93.37)	(6.63)
p-Cl-C ₆ H ₄ -	248 ^{b)}	(4.58)	77.43	4.70
	280(sh)	(4.21)	(77.42)	(5.00)
p-Br-C ₆ H ₄ -	250 ^{b)}	(4.64)	63.60	4.11
			(63.44)	(4.10)
p-NC-C ₆ H ₄ -	259	(4.45)	86.39 ^{d)}	5.30
	280(sh)	(4.37)	(87.47)	(5.24)
m-CH ₃ O-C ₆ H ₄ -	286 ^{b)}	(4.16)	84.80	6.66
			(85.24)	(6.64)
n-C ₃ H ₇ -	254	(3.84)	90.01	9.78
			(90.16)	(9.84)
n-C ₄ H ₉ -	255	(3.88)	89.68	10.54
			(89.73)	(10.27)
n-C ₅ H ₁₁ -	255	(3.88)	89.48	10.37
			(89.37)	(10.63)
n-C ₆ H ₁₃ -	255	(3.87)	88.83	10.68
			(89.07)	(10.93)
n-C ₈ H ₁₇ -	255	(3.92)	88.50	11.60
			(88.60)	(11.40)
n-C ₁₂ H ₂₅ -	255	(3.79)	87.34	12.24
			(87.95)	(12.05)

a) Analyzed as the bicycloheptyl derivatives obtained by hydrogenation (see Experimental). b) Measured in CHCl₃. c) Data from Chapter 5. d) Satisfactory analytical data was not obtained owing to instability of this compound

x,x'-di-(p-hydroxyphenyl)biscycloheptyl; 56.7% yield. Then, 0.180 g (0.476 mmol) of the bicycloheptyl was methylated with 0.20 g (1.6 mmol) of dimethyl sulfate in alkaline aqueous ethanol, by reference to the method reported by Vyas and Shah.⁶⁾ Purification of the crude product by the use of preparative thin-layer chromatography afforded 0.102 g (0.251 mmol) of x,x'-di-(p-methoxyphenyl)bicycloheptyl as a colorless oil; 52.7% yield; NMR, τ_{CCl_4} 3.2 (q, 8H, phenyl), 6.3 (s, 6H, methoxy), 7.5 (br, 4H, methine), 8.3 (br, 20H, methylene).

Found: C, 82.69; H, 9.37%. Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_2$: C, 82.71; H, 9.42%.

The reduction product of Ib was also hydrogenated in the same way to give x,x'-di-(p-methoxyphenyl)bicycloheptyl, which showed an identical infrared spectrum with that of the authentic sample described above.

Kinetic Measurements. The reaction rate of the chromous-ion reduction was measured in 10% HCl at $25.0 \pm 0.2^\circ\text{C}$ by a flow method described in the previous chapters. The products were determined by ultraviolet spectroscopy using the characteristic bands listed in Table 2.

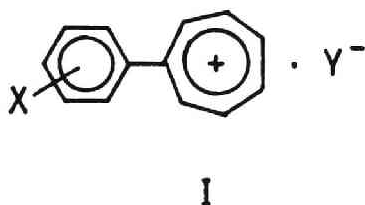
Measurements of the Charge-Transfer Bands with Pyrene. The charge-transfer spectrum was measured in 1,2-dichloroethane as reported in the preceding chapter.⁵⁾ The concentrations of pyrene and of the tropylium salts were 0.2 M and 2×10^{-3} M respectively. The precautions were taken so that the sample solution was shielded from the room light⁷⁾

and the spectrum measured immediately after the preparation of the sample.

Determination of pK_R 's. The spectrophotometric method described in the preceding chapter was followed for the determination of pK_R 's of I in 23% ethanol. As for the cations, II, the pK_R values could not be measured owing to the decomposition of II in aqueous solution with $pH \geq 1$.

Results and Discussion

Syntheses of the Tropylium-Ion Salts. Salts of the aryltropylium ions (Ia-f,h $\cdot Y^-$) were prepared according to the method of Jutz and Voithenleitner.¹⁾ p-Cyanophenyl-tropylium perchlorate (Ig $\cdot ClO_4^-$) is a new compound and



	X	Y
Ia	p-OH	BF_4
Ib	p- OCH_3	BF_4
Ic	p- CH_3	BF_4
Id	H	BF_4
Ie	p-Cl	ClO_4
If	p-Br	ClO_4
Ig	p-CN	ClO_4
Ih	m- OCH_3	ClO_4

has been synthesized by hydride abstraction from 7-(p-cyanophenyl)-1,3,5-cycloheptatriene, which in turn was prepared from 7-(p-aminophenyl)-1,3,5-cycloheptatriene by the use of Sandmeyer reaction.

Perchlorates of the n-alkyltropylium ions (II: $C_nH_{2n+1}-C_7H_6^+ \cdot ClO_4^-$; $n = 1-6, 8, 12$) were prepared, in part ($n = 3, 4, 5, 6, 8$) for the first time, in a similar manner from 7-alkyl-1,3,5-cycloheptatrienes which were synthesized by the reaction of alkylmagnesium bromides with 7-ethoxy-1,3,5-cycloheptatriene. Spectral and analytical data of II are listed in Table 1 (see Experimental). It is of interest to note that the change in mp's of these salts with the increase in the carbon number of the alkyl chain exhibits the similar tendency to that of n-alkylbenzenes, as is shown in Fig. 1.

One-Electron Reduction of the Tropylium Ions, I and II. The ions, I and II, are all readily soluble and quite stable in polar solvents such as acetonitrile and aqueous HCl except for II ($n=8, 12$) which are hardly soluble in aqueous HCl (10%) and, rather, dissolve more readily in a non-polar solvent, benzene.⁸⁾ Thus, the one-electron reduction was carried out for I and II ($n=1-6$) with five molar equivalents of Cr(II) in 10% HCl and for II ($n=8, 12$) with ten molar equivalents of zinc powder in acetonitrile. Respective tropylium ions gave the dimers of each substituted tropyli radical, i.e., x,x'-disubstituted bitropyl, in almost quantitative yields without forming any by-

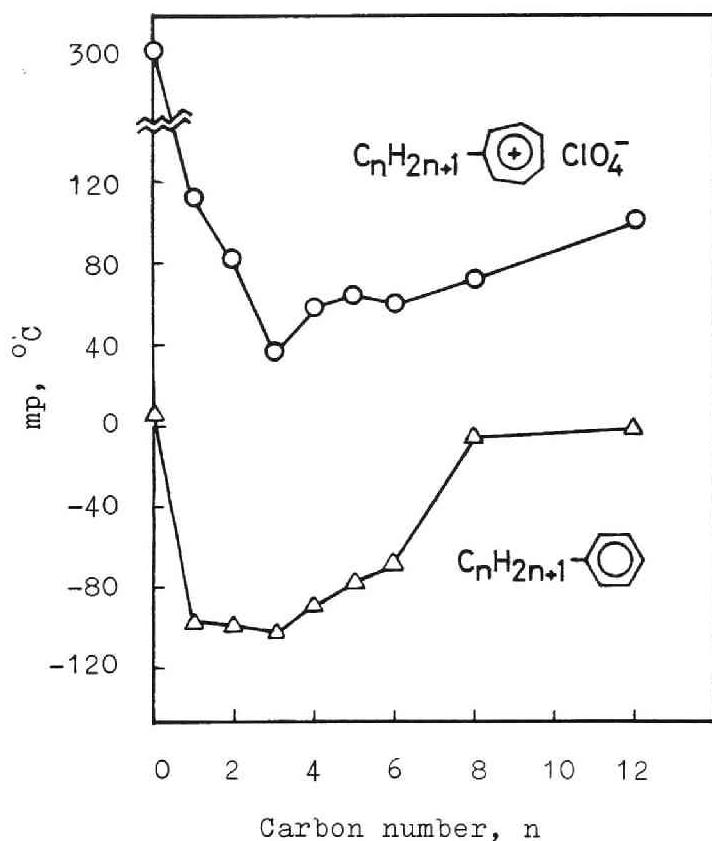


Fig. 1. The effect of the alkyl-chain length on mp's of alkyltropylm perchlorates and of alkylbenzenes. (Δ : mp's of alkylbenzenes, cited from G. Egloff, "Physical Constants of Hydrocarbons," Vol. III, Reinhold Publishing Co., N.Y. (1946))

product. The NMR spectra of the products indicated a typical pattern for a cycloheptatrienyl system together with the signals corresponding to each substituent in a similar manner as has been described in the preceding

chapter. The analytical and ultraviolet spectral data are shown in Table 2 (see Experimental).

The previous mechanistic study described in Chapter 4 indicated that the chromous ion (0.01-0.02 g-ion/l) in 10% HCl (2.9 M) is coordinated with the chloride ion and, therefore, the one-electron reduction of the carbonium ion in this solvent would proceed effectively by way of the chloride-ion bridging between the two reagents. Thus, the kinetic measurements of the chromous-ion reduction of I and II ($n=3-6$) were carried out in 10% HCl, by the use of the flow method to give the results listed in Table 3.

Correlation of the Reducibility ($\log k_2$) with the Charge-Transfer Energy. It has already been shown that the transition energy for the charge-transfer band, observed between carbonium ions and a given electron donor (e.g., pyrene), is correlated with the relative electron affinity of those cations⁹⁾ and also with $\log k_2$ for the chromous-ion reduction.⁵⁾ The cations, I and II, were also found to exhibit the charge-transfer band ($\nu_{C.T. \max}$) with pyrene as a standard electron donor (see Table 4). The correlation between $\log k_2$ and the values of $\nu_{C.T. \max}$ is reasonably good, as is shown in Fig. 2, and, thus, seems to support the assumption described in the preceding chapter that the reducibility of these ions with Cr(II) can be used as a relative criteria of electron affinity of the carbonium ion in solution.

Table 3. Second-order rate constants for the reaction of the aryl- and n-alkyltropylium ions with Cr(II) in 10% HCl at 25°C

Substituent	Initial concn.		k_2	k_2 average
	R^+	Cr(II)		
	10^{-2} g-ion/l	10^{-2} g-ion/l	l/g-ion·sec	l/g-ion·sec
p-HO-C ₆ H ₄ -	0.470	1.10	63.3	64.3
	0.497	1.06	65.2	
	0.533	0.825	64.5	
p-CH ₃ O-C ₆ H ₄ -	0.458	1.09	60.3	62.1
	0.490	0.957	64.5	
	0.510	0.947	58.7	
	0.528	0.877	64.9	
p-CH ₃ -C ₆ H ₄ -	0.323	0.910	99.0	105
	0.470	1.27	94.2	
	0.503	1.23	108	
	0.504	0.831	118	
C ₆ H ₅ - ^{a)}	0.426	0.857	140	144
	0.462	0.928	147	
p-Cl-C ₆ H ₄ -	0.248	0.549	230	237
	0.254	0.506	260	
	0.273	0.406	220	
p-Br-C ₆ H ₄ -	0.203	0.495	249	252
	0.204	0.438	283	
	0.208	0.536	256	
	0.223	0.484	221	

Table 3. (Continued)

Substituent	Initial concn		k_2	k_2 average
	R^+	Cr(II)		
	10^{-2} g-ion/l	10^{-2} g-ion/l	l/g-ion·sec	l/g-ion·sec
p-NC-C ₆ H ₄ -	0.0440	0.200	1470	1527
	0.0450	0.142	1580	
	0.0481	0.148	1530	
m-CH ₃ O-C ₆ H ₄ -	0.227	0.525	246	243
	0.211	0.502	240	
H-a)	1.80	3.05	74.1	74.0
	2.05	3.75	73.8	
CH ₃ -a)	1.99	4.12	11.1	11.1
	2.60	5.39	11.0	
	2.61	5.20	11.3	
C ₂ H ₅ -a)	2.48	4.87	9.90	10.3
	2.50	5.22	9.80	
	2.60	5.22	11.1	
C ₃ H ₇ -	0.590	1.40	11.4	11.4
	0.590	1.44	11.4	
C ₄ H ₉ -	0.440	1.53	9.52	9.69
	0.511	1.36	9.86	
	0.950	2.43	9.70	
C ₅ H ₁₁ -	0.504	1.36	10.1	10.2
	0.514	1.53	10.6	
	0.574	1.22	9.79	
C ₆ H ₁₃ -	0.401	1.26	9.90	9.14
	0.520	1.33	9.12	
	0.635	1.20	8.39	

a) Data from Chapter 5.

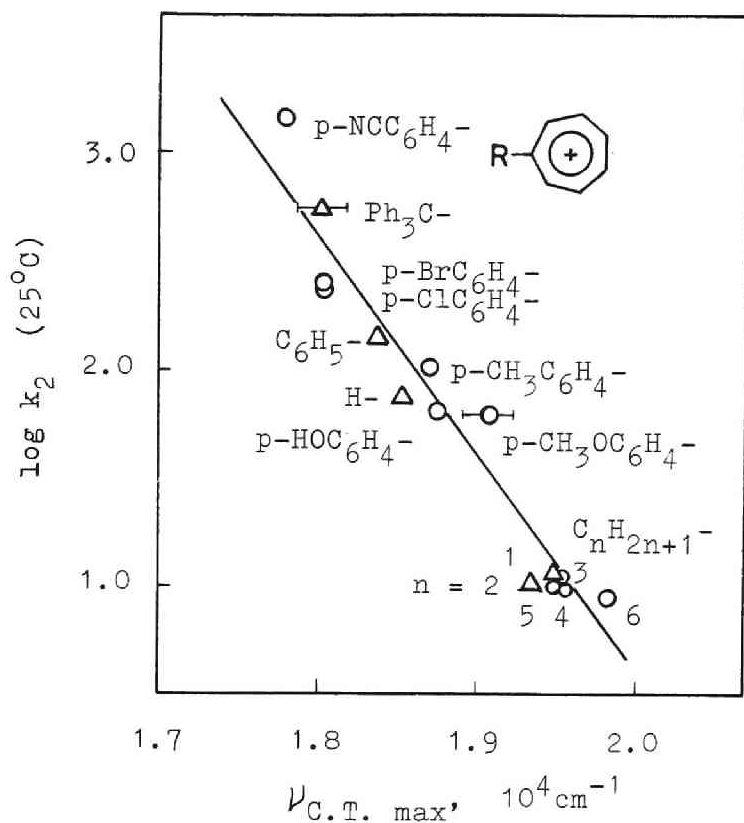


Fig. 2. The correlation of $\log k_2$ with Charge-Transfer Energy ($\nu_{C.T. \max}$).

(Δ: data described in Chapter 5)

Substituent Effects Observed in the Reduction of Aryltropylium Ions. — the Linear Free-Energy Relationship. With respect to the aryltropylium ions, I, reducibility ($\log k_2$) is also linearly correlated to the pK_R^+ values, measured spectrophotometrically in 23% ethanol

Table 4. Results of the measurements of charge-transfer bands and pK_R^+ 's of substituted tropylium ions

Substituent	$\log k_2^a)$ (25°C)	C.T. band ^{b)}		pK_R^+	
		λ_{\max} nm	ν_{\max} 10^4 cm^{-1}	Obsd. (23%EtOH)	Lit. ^{c)} (50%MeCN)
p-HO-C ₆ H ₄ -	1.808	533	1.876	5.32	4.96
p-CH ₃ O-C ₆ H ₄ -	1.793	520~ 530	1.923~ 1.887	5.17	4.59
p-CH ₃ -C ₆ H ₄ -	2.021	535	1.869	4.61	4.17
C ₆ H ₅ - ^{d)}	2.158	544	1.838	4.10	3.88
p-Cl-C ₆ H ₄ -	2.375	555	1.802	3.99	3.30
p-Br-C ₆ H ₄ -	2.402	555	1.802	3.65	3.25
p-NC-C ₆ H ₄ -	3.184	560	1.786	2.51	—
m-CH ₃ O-C ₆ H ₄	2.391	560(sh) ^{g)}		4.16	3.51
H- ^{d)}	1.869	540	1.852	4.30	4.7 ^{e)}
CH ₃ - ^{d)}	1.046	513	1.949	} f)	
C ₂ H ₅ - ^{d)}	1.013	512	1.953		
C ₃ H ₇ -	1.057	512	1.953		
C ₄ H ₉ -	0.986	511	1.957		
C ₅ H ₁₁ -	1.009	513	1.949		
C ₆ H ₁₃ -	0.961	504	1.984		

a) The logarithmic value of the averaged rate constant for the chromous-ion reduction of the respective tropylium ions.

b) Measured in 1,2-dichloroethane with pyrene as an electron donor. c) Ref. 1. d) Data from Chapter 5. e) Determined by the potentiometric titration in water (W. von E. Doering and L. H. Knox, J. Amer. Chem. Soc., 76, 3203 (1954)). f) Not determined due to the decomposition in aqueous media of pH>1.

g) Clear maximum was not observed.

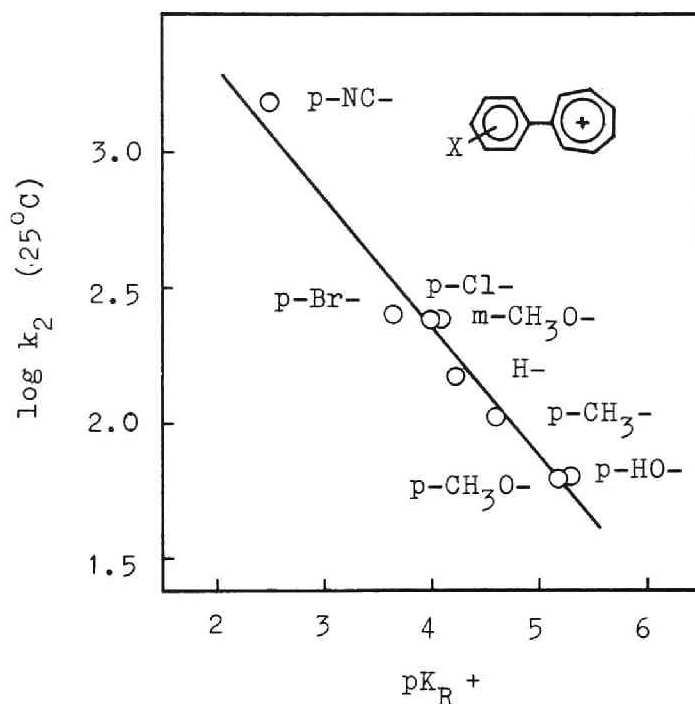


Fig. 3. The correlation of $\log k_2$ with $pK_R +$

(Table 4), as is shown in Fig.3. The electron-withdrawing substituents accelerate the reaction rate, whereas the electron-donating groups decelerate it. Thus, the Hammett plot, shown in Fig.4, gave a positive ρ -value (+1.31). The application of σ -value¹⁰⁾ gave a better linear correlation (correlation coefficient, 0.980) rather than that of σ^+ -value¹¹⁾ (correlation coefficient, 0.815) as the substituent constant. This would indicate that the

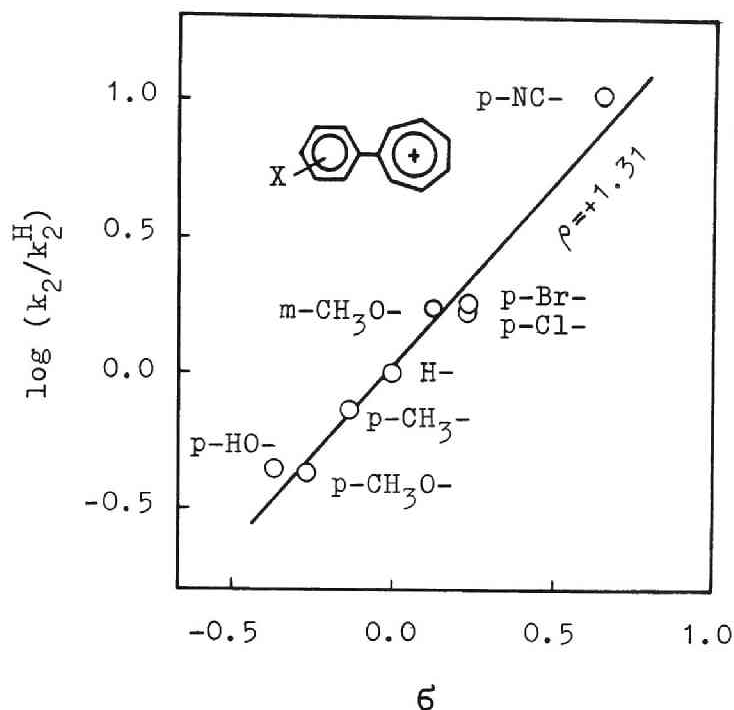


Fig. 4. The correlation of $\log k_2$ with Hammett

substituent on the phenyl group does not exert a strong conjugative effect across the phenyl group upon the tropylium ring in both the ground and transition states, in accord with the assumption that the phenyltropylium ion can not be coplanar but the planes of phenyl and tropylium rings are twisted more than 45° .^{1, 2, 12)}

Effect of the Alkyl-Chain Length upon the Reducibility of n-Alkyltropylium Ions. The results of the kinetic measurements with respect to n-alkyltropylium ions indi-

cated that the introduction of the alkyl group into the tropylium ring brings about a decrease in reducibility of the cation. The chain length of the n-alkyl substituent was found to have no remarkable effect upon the reducibility, but a slight alternation of $\log k_2$ is observed (see Table 4) with the increase in the carbon number of the n-alkyl chain. The similar alternative effect is sometimes observed in the cases of S_N2 reactions of n-alkyl halides.¹³⁾

Summary

A series of substituted phenyltropylium (I) and n-alkyltropylium ions (II) has been synthesized and kinetic measurements for the one-electron reduction of these cations with Cr(II) have been carried out in 10% HCl at 25°C. A linear correlation is observed between $\log k_2$, for I ($X-C_6H_4-C_7H_6^+$; X = p-OH, p-OCH₃, p-CH₃, H, p-Cl, p-Br, p-CN, m-OCH₃) and II ($C_nH_{2n+1}-C_7H_6^+$, n = 0, 1-6), and the transition energy of the charge-transfer band of these cations with pyrene as a donor. In addition, the values of $\log k_2$ for I exhibit a good linear free energy relationship with pK_R^+ and also with σ -value ($\rho=+1.31$), rather than with σ^+ . The n-alkyl group is shown to diminish the reducibility of the tropylium ion and a slight rate alternation effect of the length of the n-alkyl chain is observed.

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Chapter 7 The Reducibility of the Hetero-Substituted Tropylium Ions as Studied by the Competitive Reduction with Zinc

Introduction

Throughout the studies described in Chapters 5 and 6, the tropylium ion was chosen as a standard substrate for kinetic study on the chromous-ion reduction. Especially with respect to the substituted phenyltropylium ions, the existence of the Hammett linear free-energy relationship was observed. Thus, as an extension of this study, it seems of interest to synthesize a series of tropylium ions with a variety of hetero-atom substituents directly bonded to the ring and to investigate on the much wider variation of reactivity brought about by these substituents.

However, the previous method of the chromous-ion reduction is not applicable to the hetero-atom substituted tropylium ions owing to the instability of these cations in "aqueous" media; on the other hand, acetonitrile in which these cations are stable can not be a good solvent for the chromous ion. Hence, it was attempted to estimate the relative reducibility of the hetero-atom substituted tropylium ions by the use of the competitive reduction with zinc powder in "anhydrous" acetonitrile. The use of zinc

powder as a one-electron reductant for the carbonium ions has been well documented¹⁾ since the first observation of the zinc reduction of the tropylium ion to give bitropyl reported by Doering and Knox.^{1a)} In addition, the formation of the radical species (the tropyl radical) in the course of the zinc reduction of the tropylium ion has been proved with the radical trapping technique, as has been described in Chapter 3.

In this chapter will be made some discussion on the effect of hetero-atom substituents upon the reducibility of the tropylium ions and, also, on the correlation of the reducibility with the electron affinity, on the basis of the relative reduction-rate measured by the competitive reduction method.

Experimental²⁾

Materials. All the reagents employed were of a reagent-grade quality. Acetonitrile and ethyl acetate were refluxed and distilled over phosphorus pentoxide; acetonitrile, bp 80.5-81.1°C; ethyl acetate, bp 75.5-76.5°C. Carbon tetrachloride, chloroform, and 1,2-dichloroethane were refluxed and distilled over calcium chloride; carbon tetrachloride, bp 75.0-75.5°C; chloroform, bp 60.0-60.3°C; 1,2-dichloroethane, bp 83.0-83.4°C. Tetrahydrofuran (THF) was distilled over lithium aluminum hydride,

bp 66.1-66.4°C.

Chloro-³⁾ (III), methoxy-⁴⁾ (VI), diethylamino-⁵⁾ (VII), and t-butylamino-⁵⁾ (VIII) tropylium perchlorates were prepared according to the methods reported in the literatures; III, mp 175.0-176.0°C (lit, mp 172-173°C³⁾); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 232 nm (ϵ , 37200) 308 nm (9100) (lit, $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 232 nm ($\log \epsilon$, 4.57), 308 nm (3.96)³⁾); VI, mp 107.0-107.5°C (lit, mp 107.5°C⁴⁾), $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 232 nm (ϵ , 34700), 313 nm (11000) (lit, $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 232 nm ($\log \epsilon$, 4.54) 313 nm (4.04)⁴⁾); VII, mp 68.0-72.0°C (lit, mp 75-76°C⁵⁾), $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 241 nm (ϵ , 20000) (lit, $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 241 nm ($\log \epsilon$, 4.30) 335 nm (4.21)⁵⁾); VIII, mp 111.5-112.0°C (lit, mp 112-113°C⁵⁾), $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 239 nm (ϵ , 18400), 242.5 nm (18400), 333 nm (13000) (lit, $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 237 nm ($\log \epsilon$, 4.35), 330 nm (4.18)⁵⁾).

Phenyl- (IX) and unsubstituted tropylium (X) fluoroborates and t-butyltropylium perchlorate (XI) were obtained by the method described in Chapter 5.

Synthesis of Cyanotropylium Perchlorate (I).

7-Cyano-1,3,5-cycloheptatriene^{1a)} was heated in an evacuated ampoule at 175°C for 1.5 hr and distilled under reduced pressure to give a mixture of 3- and 1-cyano-1,3,5-cycloheptatrienes; bp 86.5-90.0°C/5 mmHg. To a solution of 3.498 g (29.8 mmol) of the isomeric mixture of cyanocycloheptatrienes in 7.7 ml of acetonitrile was added 10.231 g (29.8 mmol) of triphenylmethyl (trityl) perchlorate. The mixture was magnetically stirred at 60°C for 1 hr and then

at 80°C for 5 min; the most of the crystals of trityl perchlorate disappeared and the mixture turned dark red. After an addition of 26 ml of ethyl acetate, the mixture was cooled to 0°C. The pale yellow crystals that separated out were collected by filtration, washed successively with ethyl acetate and ether, and dried in vacuo to give 4.885 g (22.7 mmol) of I; 76.2% yield. I was purified by recrystallization from acetonitrile-ethyl acetate for the analyses; mp 158.0°C (decomposition with violent explosion); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 293 nm (ϵ , 6610), 298 nm (6450); NMR, $\tau_{\text{CF}_3\text{COOH}}$ 0.4 (s, tropylium ring); $\nu_{\text{max}}^{\text{KBr}}$ 740, 870, 940, 955, 1080-1150, 1380, 1440, 1480, 1525, 1595, 1630, 2220, 3020 cm^{-1} .

Found: C, 44.34; H, 2.81%. Calcd for $\text{C}_8\text{H}_6\text{NO}_4\text{Cl}$: C, 44.57; H, 2.81%.

Synthesis of Carbomethoxytropylium Perchlorate (II).

7-Carbomethoxy-1,3,5-cycloheptatriene⁶⁾ was thermally isomerized at 175°C for 1.5 hr to give a mixture of 3- and 1-carbomethoxy-1,3,5-cycloheptatrienes; bp 74.0-77.0°C/3 mmHg. In 6.4 ml of acetonitrile, 3.509 g (23.4 mmol) of the mixture of carbomethoxycycloheptatrienes was allowed to react with 8.012 g (23.3 mmol) of trityl perchlorate with magnetic stirring at 60°C for 6 min; the trityl salt disappeared almost instantaneously when the mixture was heated and instead pale yellow crystals separated. After addition of 24 ml of ethyl acetate, the mixture was cooled to 0°C and then filtered to give 5.427 g (21.8 mmol) of II as pale yellow crystals; 93.4% yield; mp 143.0-143.3°C, after

recrystallization from acetonitrile-ethyl acetate; $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 225.5 nm (ϵ , 43000), 286 nm (4660); NMR, $\tau_{\text{CF}_3\text{COOH}}$ 0.0 (m, 2H, tropylium ring), 0.5 (m, 4H, tropylium ring), 5.7 (s, 3H, methyl); $\nu_{\text{max}}^{\text{KBr}}$ 680, 740, 760, 805, 870, 925, 940, 970, 1070-1150, 1250, 1270, 1290, 1350, 1370, 1440, 1480, 1615, 1730, 2960, 3015 cm^{-1} .

Found: C, 43.21; H, 3.58%. Calcd for $\text{C}_9\text{H}_9\text{O}_6\text{Cl}$: C, 43.48; H, 3.65%.

Synthesis of Methylthiotropylium Perchlorate (V).

To a magnetically stirred solution of 10.356 g (58.1 mmol) of tropylium fluoroborate in 110 ml of 0.1N HCl, there was added 9.5 g of 30% methanolic solution of methylmercaptan (58.7 mmol); a slightly exothermic reaction took place and the solution turned yellow. After stirring for 20 min at room temperature, the turbid solution was extracted with three 100 ml-portions of ether, washed with 10% NaCl and dried over MgSO_4 . The ethereal solution, after distillation and evaporation, gave 4.309 g (31.2 mmol) of 7-methylthio-1,3,5-cycloheptatriene as a pale yellow oil; 53.6% yield; bp $74.0^\circ\text{C}/5$ mmHg; NMR, τ_{CCl_4} 3.5 (t, 2H, $\text{H}^{3,4}$), 3.9 (m, 2H, $\text{H}^{2,5}$), 4.7 (d of d, 2H, $\text{H}^{1,6}$), 6.9 (t, 1H, H^7), 7.9 (s, 3H, methyl).

Found: C, 69.72; H, 7.42%. Calcd for $\text{C}_8\text{H}_{10}\text{S}$: C, 69.51; H, 7.29%.

A solution of 2.092 g (15.1 mmol) of the isomeric mixture of methylthiocycloheptatrienes, obtained by the thermal isomerization described above (bp, 50.0 - $61.0^\circ\text{C}/$

4 mmHg), in 10 ml of acetonitrile was added to a magnetically-stirred suspension of 5.205 g (15.2 mmol) of trityl perchlorate in 10 ml of acetonitrile over a 2-min period at room temperature. During the addition the reaction temperature rose from 22.5°C to 30.0°C and all the trityl salt dissolved to give a dark red solution. After stirring for 15 min at room temperature, 100 ml of ethyl acetate was added and the mixture was cooled at 0°C. The yellow crystals that separated out were collected, washed, and dried as described above to give 2.860 g (12.1 mmol) of V; 80.0% yield; mp 114.0-115.0°C (lit, mp 114-115°C³); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 219.5 nm (ϵ , 23300), 260 nm (17000), 380 nm (19800) (lit, $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 258 nm (ϵ , 14800), 378 nm (ϵ , 17400)³); $\nu_{\text{max}}^{\text{KBr}}$ 740, 845, 1040-1120, 1225, 1235, 1280, 1325, 1370, 1420(sh), 1430, 1470, 1510, 1600, 1615, 2910, 3010 cm⁻¹.

Synthesis of 7-Triphenylsilyl-1,3,5-cycloheptatriene.

To a stirred solution of 5.791 g (45.9 mmol) of 7-ethoxy-1,3,5-cycloheptatriene in 20 ml of THF, there was added 130 ml of a THF solution of triphenylsilyllithium, prepared from 15.0 g (51.0 mmol) of triphenylsilyl chloride and 1.40 g (0.202 g-atom) of lithium according to the method of Gilman et al., ⁷) by the use of a hypodermic syringe over a 25-min period at room temperature; the reaction temperature rose from 25.0°C to 35.0°C and the dark reddish-brown color of triphenylsilyllithium, which was, at the beginning, instantaneously discharged on addition to the ethoxycycloheptatriene solution, began to remain during the

course of addition. The dark brown mixture with white precipitates was stirred at room temperature for 2.5 hr and let stand overnight. Then, 150 ml of 10% HCl was cautiously added and the mixture was worked up in the usual way to give 17.5 g of a partially solidified yellowish oil, from which, upon recrystallization from benzene, was separated 0.451 g (0.836 mmol) of hexaphenyldisilane as white crystals; mp 355-360°C (lit, mp 361-362°C⁷); an identical infrared spectrum with that of the authentic sample. The mother liquor was concentrated in vacuo and the residual solid, upon recrystallization from ethanol, gave 3.338 g (9.53 mmol) of 7-triphenylsilyl-1,3,5-cycloheptatriene as white crystals; mp 152.0-155°C with slow resolidification, presumably due to the formation of 3-triphenylsilyl isomer which eventually melts at 178°C; NMR, τ_{CCl_4} 2.6 (m, 15H, phenyl), 3.4 (t, 2H, H^{3,4}), 3.7 (m, 2H, H^{2,5}), 4.8 (d of d, 2H, H^{1,6}), 8.2 (t, 1H, H⁷).

Found: C, 85.48; H, 6.07%. Calcd for C₂₅H₂₂Si: C, 85.66; H, 6.33%.

The filtrate of the recrystallization, upon evaporation gave 12.260 g of a yellowish solid, which was then chromatographed over 310 g of silica gel (Nakarai, No. II-A, 100-200 mesh). From the fractions eluted with n-hexane-benzene (9:1~6:1) was obtained a mixture of 0.163 g (0.898 mmol) of bitropyl and 0.340 g (0.131 mmol) of triphenylsilane; the composition was determined by the NMR analysis, whereas the identities established by the use of thin-layer

chromatography and from the comparison of the NMR spectrum of the mixture with those of the authentic samples. From the fractions eluted with n-hexane-benzene (4:1~3:1) was isolated 4.654 g (13.3 mmol) of 7-triphenylsilyl-1,3,5-cycloheptatriene, whereas the successive fractions eluted with n-hexane-benzene (2:1) gave 0.657 g (1.22 mmol) of hexaphenyldisilane after recrystallization from chloroform. In addition, the fractions eluted with benzene-ether (1:1) afforded 3.364 g (12.2 mmol) of triphenylsilanol after recrystallization from benzene; mp 152-155°C (lit, mp 153-155°C⁷).

Thus, the yields of each isolated product are summarized as follows: bitropyl, 3.9%; 7-triphenylsilyl-1,3,5-cycloheptatriene, 47.5%; the tropylium ion, 21.2% (determined from the ultraviolet spectrum of the aqueous layer); hexaphenyldisilane, 4.8% (based on triphenylsilyl chloride); triphenylsilane, 2.6% (vide supra); triphenylsilanol, 24.1% (vide supra).

7-Triphenylsilyl-1,3,5-cycloheptatriene was sealed in a Pyrex tube under vacuum and heated at 200°C for 30 min. The thin-layer chromatography analysis of the recovered sample indicated the presence of the isomeric mixture of triphenylsilylcycloheptatrienes but no spot corresponding to bitropyl was detected.

Synthesis of Triphenylsilyltropylium Perchlorate (IV).

7-Triphenylsilyl-1,3,5-cycloheptatriene was thermally isomerized at 150°C for 5 hr to give 3-triphenylsilyl-1,3,5-

cycloheptatriene; NMR, τ_{CCl_4} 2.6 (m, 15H, phenyl), 3.1 (d, 1H, H⁴), 3.7 (m, 2H, H^{2,5}), 4.5 (m, 2H, H^{1,6}), 7.7 (t, 2H, H⁷). A suspension of 0.638 g (1.82 mmol) of 3-triphenylsilyl-1,3,5-cycloheptatriene and 0.634 g (1.85 mmol) of trityl perchlorate in 10 ml of acetonitrile was magnetically stirred at 55°C for 30 min and at 80°C for 5 min to give a dark red solution. After addition of 100 ml of ethyl acetate, the solution was cooled to 0°C. The glittering, brownish crystals that separated out were collected in the usual way to give 0.702 g (1.57 mmol) of IV; 86.0% yield. Recrystallization from acetonitrile-ethyl acetate gave mp 188.0°C (decomposition with explosion); $\lambda_{\text{max}}^{\text{CH}_3\text{CN}}$ 218 nm (ϵ , 65000), 265 nm (sh) (6960), 271.5 nm (6800), 281 nm (6500); NMR, $\tau_{\text{CF}_3\text{COOH}}$ 0.5-0.8 (m, 6H, tropylium ring), 2.5 (s, 15H, phenyl); $\nu_{\text{max}}^{\text{KBr}}$ 680, 700, 715, 745(sh), 750, 870, 940, 1000, 1030, 1070-1120, 1160, 1190, 1240, 1250, 1265, 1380, 1430, 1440(sh), 1485, 1590, 3020, 3050, 3080 cm^{-1} .

Found: C, 66.80; H, 4.52%. Calcd for $\text{C}_{25}\text{H}_{21}\text{ClSi}$: C, 66.88; H, 4.72%.

One-Electron Reduction of the Substituted Tropylium Ions with Zinc Powder. To a magnetically stirred solution of 0.500 g (2.01 mmol) of II in 20 ml of acetonitrile, there was added 1.315 g (20.1 mg-atom) of zinc powder. The mixture was stirred for 10 min at room temperature under an atmosphere of nitrogen. The excessive zinc was filtered off and 40 ml of CCl_4 and 40 ml of water were added to the filtrate, which was then worked up in the usual

way to give 0.317 g (1.06 mmol) of x,x'-dicarbomethoxy-bitropyl as a viscous oil; 105.6% yield; NMR, τ_{CCl_4} 2.2-4.7 (m, 10H, olefinic ring protons), 6.1 and 6.2 (s, 6H, methyl), 8.0 (br, 2H, methine).

Reductions of I, III, IV, V, VI, IX, X, and XI were carried out in the same way to give the di-substituted bitropyl in the yields of 90-105%. The ultraviolet-spectral and analytical data of all the products are tabulated in Table 1.

Under the same reaction conditions, 0.0557 g (0.239 mmol) of VII was allowed to react with 0.160 g (2.46 mg-atom) of zinc powder in 2 ml of acetonitrile. After filtration, 20 ml of ether was added to the filtrate and the white precipitates which were formed were collected to give 0.0503 g (0.216 mmol) of unchanged VII; 90.4% recovery. The ethereal filtrate gave 0.0015 g of an unidentified oil. An attempted reduction of VIII, with the same procedures, also resulted in 106% recovery of unchanged VIII.

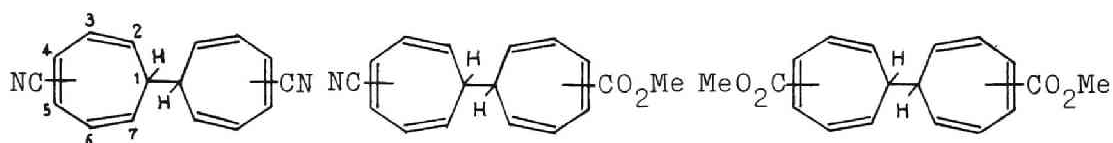
Competitive Reduction. With respect to the competitive reduction of the cations, I, II, III, IV, IX, and X, the details of the procedures are illustrated by the following description of a representative run (Run No. 1-3) for the competition of I and II. In a 25-ml, four-necked flask equipped with a thermometer, a magnetic-stirring bar, and nitrogen inlet and outlet, which was immersed in a water bath thermostated at 25.0°C, there was stirred a solution of 0.108 g (0.502 mmol) of I and 0.125 g (0.503 mmol) of

Table 1. Ultraviolet spectral and analytical data for
x,x'-disubstituted bitropyls^{a)}

Substituent	UV		Elemental analysis	
	$\lambda_{\text{max}}^{\text{EtOH}}$	(ϵ)	Found (Calc'd)	
	nm		C%	H%
NC-	263	(6340)	82.60	5.47
			(82.73)	(5.21)
CH ₃ O ₂ C-	223.5	(37100)	71.73	6.01
			(72.47)	(6.08)
Cl-	261	(6800)	66.94	4.81
			(66.95)	(4.82)
(C ₆ H ₅) ₃ Si-	255.5	(11800)	85.73	6.10
	261	(11820)	(85.91)	(6.06)
	265(sh)	(11050)		
CH ₃ S-	302	(8800)	70.06	6.84
			(70.02)	(6.61)
CH ₃ O-	250.5	(6580)	79.08	7.50
	285	(5270)	(79.31)	(7.49)

a) As for the data for diphenyl-, di-t-butyl-, and unsubstituted bitropyls, see Chapter 5.

II in 5.0 ml of acetonitrile. To this solution was added 0.0205 g (0.314 mg-atom) of zinc powder and the mixture was stirred under nitrogen atmosphere for 10 min. The reaction appeared to be very fast, completing in less than 1 min, as indicated by the rapid disappearance of the zinc powder. The solution was evaporated to dryness under reduced pressure. The residual oily solid was then extracted with 25 ml of carbon tetrachloride in five portions. The carbon tetrachloride solution was washed with three 35-ml portions of water, dried over MgSO_4 , and evaporated to give 0.0644 g of a colorless oil, which was then analyzed with NMR as follows; regarding the product oil as the mixture of substituted bitropyls such as:



the molar ratio of the cyanotropyl and carbomethoxytropyl groups were determined to be 2.85: 1.00, from the relative values of integrated intensities (average of 5 measurements) for the signals corresponding to the methyl protons and the total olefinic ring protons (H^{2-7}). From this molar ratio and the weight of the product mixture, the radical yield was calculated to be 76.0% for the reduction of I and 26.7% for the reduction of II. On the other hand, the residual solid from carbon tetrachloride extraction was dissolved in acetonitrile and subjected to the ultraviolet spectroscopy. The amounts of unchanged cations, I and II, were

determined to be 7.53 mmol (15.0% recovery) and 3.36 mmol (66.7% recovery), respectively, by the use of the absorbance and the molar extinction coefficient of respective cations at the wavelengths corresponding to the maximum absorptions of individual cations, assuming the additivity of the absorbance of the respective cations at each wavelength.

With respect to the cations, V, VI, X, and XI, exactly the same method was adopted except the following procedures; after the reaction, 20 ml of 10% HCl was added to the reaction mixture and the products were extracted with ether, worked up, and analyzed as described above, while the unchanged cations were determined from the ultraviolet spectrum of the acidic aqueous layer.

The results of the competitive reduction are listed in Table 2. The validity of the analytical methods mentioned above is verified by the fairly good material balance (90~110%) obtained in each case, as is shown in the Table.

Measurements of the Charge-Transfer Bands with Pyrene.

The charge-transfer spectra were measured in 1,2-dichloroethane as described in previous chapters. The concentrations of a donor (pyrene) and of an acceptor (the substituted tropylium ion) were 0.2 M and 2×10^{-3} M, respectively. The previously-described precautions were taken against the light and the spectrum was measured immediately after preparation of the sample solution.

Table 2. Results of the competitive reduction of the
hetero-atom substituted tropylium ions ($X-C_7H_6^+$) with
zinc at 25°C. a)

Run [#]	Zn	$X-C_7H_6^+$	Radical Yield	Cation Recov.	Balance	$-\log \frac{[X-C_7H_6^+]}{[X-C_7H_6^+]_0}$	k_A/k_B
	mg-atom		%	%	%		
Competition of $NC-C_7H_6^+(A)$ vs. $CH_3O_2C-C_7H_6^+(B)$							
1-1	0.200	{ A	41.7	42.7	84.4 ^{b)}	0.234	4.71
		{ B	10.8	89.8	100.6	0.050	
1-2	0.251	{ A	50.7	26.9	77.6 ^{b)}	0.407	4.42
		{ B	19.1	80.0	99.1	0.092	
1-3	0.314	{ A	76.0	15.0	91.0	0.620	4.59
		{ B	26.7	66.7	93.4	0.135	
$(k_A/k_B)_{Aver.} = 4.57$							
Competition of $CH_3O_2C-C_7H_6^+(A)$ vs. $Cl-C_7H_6^+(B)$							
2-1	0.210	{ A	46.1	52.5	98.6	0.268	2.03
		{ B	26.2	69.0	95.2	0.132	
2-2	0.248	{ A	50.2	49.0	99.2	0.303	2.13
		{ B	27.9	74.3	102.2	0.142	
2-3	0.252	{ A	50.2	43.4	93.6	0.303	2.26
		{ B	26.5	92.0	118.5	0.134	
2-4	0.294	{ A	67.6	36.0	103.6	0.489	2.00
		{ B	43.0	53.8	96.8	0.244	
$(k_A/k_B)_{Aver.} = 2.11$							
Competition of $Cl-C_7H_6^+(A)$ vs. $Ph_3Si-C_7H_6^+(B)$							
3-1	0.188	{ A	36.1	48.6	94.7	0.194	2.37
		{ B	17.2	81.8	99.0	0.082	
3-2	0.220	{ A	45.1	50.0	95.6	0.260	2.32
		{ B	22.7	64.3	87.0	0.112	

Table 2. (Continued)

Run [#]	Zn	X-C ₇ H ₆ ⁺	Radical Yield	Cation Recov.	Balance	$-\log \frac{[X-C_7H_6^+]}{[X-C_7H_6^+]_0}$	k _A /k _B
	mg-atom		%	%	%		

3-3	0.257	{	A	55.0	42.8	97.8	0.347	1.99
		{	B	33.0	60.0	93.0	0.174	
								$(k_A/k_B)_{\text{Aver.}} = 2.23$

Competition of Ph₃Si-C₇H₆⁺(A) vs. C₇H₇⁺(B)

4-1	0.203	{	A	57.4	51.0	108.4	0.371	}	4.08
			B	16.3	81.8	98.1	0.077		
4-2	0.254	{	A	46.5	47.5	94.0	0.272	}	5.17
			B	11.4	82.1	93.5	0.053		
4-3	0.255	{	A	47.5	52.7	100.2	0.280	}	4.52
			B	13.3	89.6	102.9	0.062		
4-4	0.285	{	A	72.1	39.5	111.6	0.554	}	5.23
			B	21.7	75.3	97.0	0.106		
$(k_A/k_B)_{\text{Aver.}} = 4.93$									

Competition of Ph-C₇H₆⁺(A) vs. C₇H₇⁺(B)

5-1	0.248	{	A	41.4	51.4	92.8	0.232	}	2.58
			B	18.7	81.9	100.6	0.090		
5-2	0.249	{	A	51.0	49.6	100.6	0.310	}	2.52
			B	24.7	70.7	95.4	0.123		
5-3	0.250	{	A	58.0	47.0	105.0	0.377	}	2.64
			B	28.1	68.7	96.8	0.143		
5-4	0.251	{	A	35.8	63.0	98.8	0.192	}	2.24
			B	18.0	82.6	100.6	0.086		
$(k_A/k_B)_{\text{Aver.}} = 2.50$									

Table 2. (Continued)

Run#	Zn	X-C ₇ H ₆ ⁺	Radical Yield	Cation Recov.	Balance	$-\log \frac{[X-C_7H_6^+]}{[X-C_7H_6^+]_0}$	k _A /k _B
	mg-atom		%	%	%		
Competition of C ₇ H ₇ ⁺ (A) vs. CH ₃ S-C ₇ H ₆ ⁺ (B)							
6-1	0.203	{ A	36.3	70.3	106.6	0.196	} 3.47
		{ B	12.2	81.2	93.4	0.057	
6-2	0.242	{ A	71.3	31.0	102.6	0.542	} 4.11
		{ B	26.3	71.7	98.0	0.132	
6-3	0.249	{ A	61.6	40.4	102.0	0.416	} 3.85
		{ B	22.0	65.1	87.1	0.108	
6-4	0.249	{ A	64.5	43.7	108.2	0.450	} 4.02
		{ B	22.7	68.2	90.9	0.112	
6-5	0.251	{ A	68.2	32.0	100.2	0.498	} 4.12
		{ B	24.3	64.2	88.5	0.121	
(k _A /k _B) _{Aver.} = 3.91							
Competition of CH ₃ S-C ₇ H ₆ ⁺ (A) vs. t-C ₄ H ₉ -C ₇ H ₆ ⁺ (B)							
7-1	0.113	{ A	26.8	68.4	95.2	0.135	} 1.61
		{ B	17.6	85.6	103.2	0.084	
7-2	0.119	{ A	29.4	66.0	95.4	0.151	} 1.68
		{ B	18.8	79.8	98.6	0.090	
7-3	0.122	{ A	29.8	63.0	92.8	0.154	} 1.64
		{ B	19.4	81.0	100.4	0.094	
7-4	0.249	{ A	58.2	38.8	97.0	0.370	} 1.80
		{ B	38.4	57.8	96.2	0.210	
7-5	0.249	{ A	56.1	41.2	97.3	0.358	} 1.90
		{ B	35.2	60.8	96.0	0.188	
7-6	0.249	{ A	58.0	39.0	97.0	0.377	} 1.76
		{ B	38.9	60.7	99.6	0.214	
7-7 ^c)	0.503	{ A	48.2	44.3	92.5	0.286	} 1.87
		{ B	29.7	71.1	100.8	0.153	

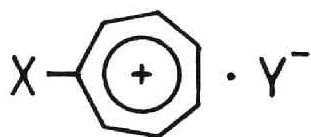
Table 2. (Continued)

Run [#]	Zn	X-C ₇ H ₆ ⁺	Radical Yield	Cation Recov.	Balance	$-\log \frac{[X-C_7H_6^+]}{[X-C_7H_6^+]_0}$	k_A/k_B
	mg-atom		%	%	%		
7-8 ^{d)}	0.505	{ A	28.2	68.1	96.3	0.144	} 1.76
		{ B	17.2	86.2	103.4	0.082	
7-9 ^{e)}	0.512	{ A	42.3	56.9	99.2	0.239	} 1.74
		{ B	27.2	77.5	104.7	0.138	
7-10 ^{f)}	1.02	{ A	54.1	49.1	103.2	0.338	} 1.69
		{ B	36.9	69.9	106.8	0.200	
$(k_A/k_B)_{Aver.} = 1.75$							
Competition of t-C ₄ H ₉ -C ₇ H ₆ ⁺ (A) vs. CH ₃ O-C ₇ H ₆ ⁺ (B)							
8-1	0.249	{ A	54.6	40.3	94.9	0.343	} 5.20
		{ B	14.0	67.3	81.3	0.066	
8-2	0.249	{ A	57.7	31.3	89.0	0.374	} 4.93
		{ B	16.0	72.9	88.9	0.076	
8-3	0.249	{ A	61.4	43.0	104.4	0.413	} 4.85
		{ B	17.8	57.3	75.1	0.085	
8-4	0.283	{ A	71.6	21.5	93.1	0.547	} 4.88
		{ B	22.8	61.8	84.6	0.112	
$(k_A/k_B)_{Aver.} = 4.97$							

- a) Solvent: acetonitrile, 5 ml. Initial concentration of each cation: 0.10 M. Reaction time: 10 min.
- b) The relatively poor value of the material balance is probably due to partial decomposition of the unchanged NC-C₇H₆⁺ during UV spectroscopy, caused by moisture in the solvent.
- c) Reaction time: 1.2 min.
- d) Reaction time: 0.6 min.
- e) Reaction time: 0.9 min.
- f) Reaction time: 0.2 min.

Results and Discussion

Syntheses of the Hetero-Atom Substituted Tropylium
Ions. Among the perchlorates of the hetero-atom substituted tropylium ions, I-VIII, those of the chloro-³⁾ (III), methoxy-⁴⁾ (VI), diethylamino-⁵⁾ (VII), and t-butylamino-⁵⁾ (VIII) derivatives were prepared according to the literatures. Cyano- (I), carbomethoxy- (II), and methylthio-tropylium³⁾ (V) perchlorates were synthesized by the hydride abstraction from the corresponding 3-substituted 1,3,5-cycloheptatrienes, which had been obtained from the 7-substituted derivatives⁸⁾ by thermal isomerization. Triphenylsilyltropylium perchlorate (IV) was synthesized in the same way from 7-triphenylsilyl-1,3,5-cycloheptatri-



	X	Y
I	-CN	ClO ₄
II	-CO ₂ CH ₃	ClO ₄
III	-Cl	ClO ₄
IV	-Si(C ₆ H ₅) ₃	ClO ₄
V	-SCH ₃	ClO ₄
VI	-OCH ₃	ClO ₄
VII	-N(C ₂ H ₅) ₂	ClO ₄
VIII	-NH-t-C ₄ H ₉	ClO ₄
IX	-C ₆ H ₅	BF ₄
X	-H	BF ₄
XI	-t-C ₄ H ₉	ClO ₄

ene, which had been obtained by the reaction of 7-ethoxy-1,3,5-cycloheptatriene with triphenylsilyllithium.⁷⁾

Among these salts, I,⁹⁾ II, and IV are new compounds.

Previously, we have observed a homolytic dissociation of 7-triphenylmethyl-1,3,5-cycloheptatriene into the tropylium (cycloheptatrienyl) and triphenylmethyl radicals by the ESR measurement at 60-95°C.¹⁰⁾ Larrabee¹¹⁾ has also reported that 7-triphenylstannic-1,3,5-cycloheptatriene undergoes a similar thermal cleavage at 160°C and observed a fluxional behavior of the triphenylstannic group around the seven-membered ring from the NMR measurement at 0-139°C. The ease of these homolytic cleavages would be attributed to the considerable resonance-stabilization of the "symmetrical" tropylium radical.¹²⁾ However, in spite of the close similarity of the structure, 7-triphenylsilyl-1,3,5-cycloheptatriene does not exhibit such a behavior: It does not show any evidence for bitropylium formation when heated at 200°C, indicating the reluctance of carbon-silicon bond against the homolytic dissociation.

Competitive Reduction. First, the one-electron reduction of each single cation with an excess (twenty-fold of the theoretical amount) of zinc powder was carried out in acetonitrile for ten minutes. Almost quantitative formation of the x,x'-disubstituted bitropylium was confirmed, except for the aminotropylium ions, VII and VIII, which were not reduced and recovered unchanged under these reaction conditions. This indicates the exceptional stability

due to the electron donation by the amino group. The analytical and ultraviolet-spectral data of x,x'-disubstituted bitropyls are tabulated in Table 1 (see Experimental).

Then, the competitive reduction was conducted as follows. Each pair of an equal amount of cations (R_A^+ , R_B^+) was subjected to a competitive reduction in acetonitrile at 25°C with zinc powder $\frac{1}{4}$ - $\frac{1}{2}$ of the theoretical amount required for the complete reduction of a single cation. The mixture of the coupling product of the radicals formed from both cations (i.e., R_A-R_A , R_A-R_B , and R_B-R_B) was extracted. The yield of each radical was determined from the total weight of the coupling-product mixture and the NMR analysis.¹³⁾ In each case, the material balance of the reduction with respect to each cation was found to be 90-110% from the ultraviolet spectroscopy of the unchanged cation. When we assume the first-order dependency of the reaction rate on the cation concentration, the ratio of rate constants for the competing cations is expressed by the following equation:¹⁴⁾

$$k_A/k_B = \log([R_A^+]/[R_A^+]_0)/\log([R_B^+]/[R_B^+]_0)$$

where $[R_A^+]_0$ and $[R_B^+]_0$ denote the initial concentrations of the cations, R_A^+ and R_B^+ , respectively. The appropriateness for the application of this equation to the present case was verified by the linearity of the plot of $\log([R_A^+]/[R_A^+]_0)$ against $\log([R_B^+]/[R_B^+]_0)$ through the point

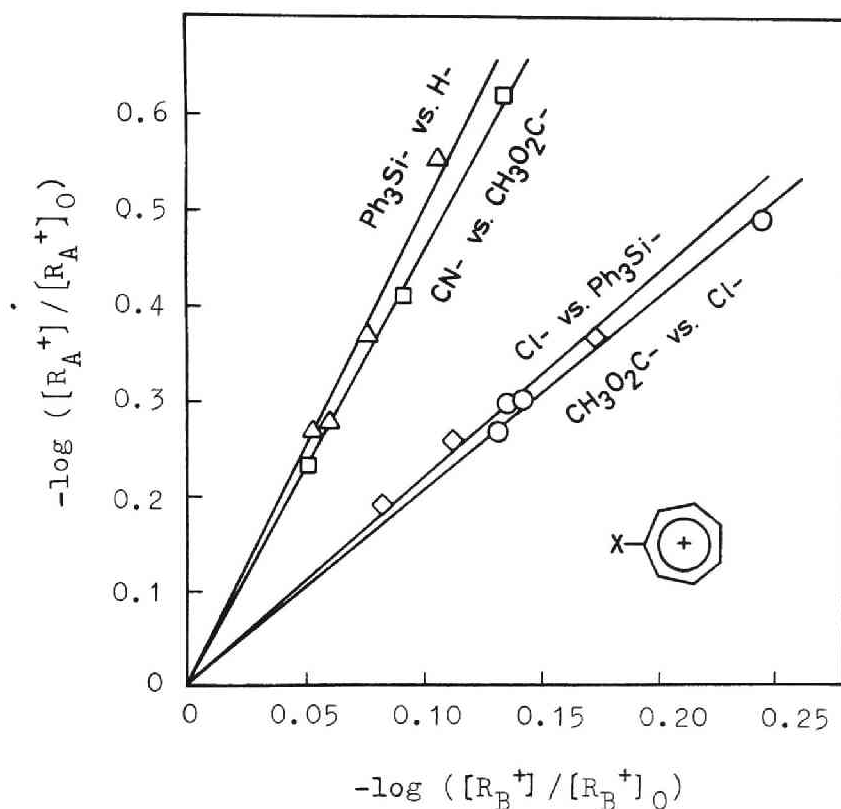


Fig. 1. Plot of $-\log ([R_A^+]/[R_A^+]_0)$ vs. $-\log ([R_B^+]/[R_B^+]_0)$ for the competitive reduction of NC^- , $\text{CH}_3\text{O}_2\text{C}^-$, Cl^- , $(\text{C}_6\text{H}_5)_3\text{Si}-\text{C}_7\text{H}_6^+$ and C_7H_7^+ with zinc in acetonitrile at 25°C.

of origin, with regard to each cation pair, as is shown in Figs. 1 and 2. From the slope of each straight line, the relative rate constant ($k_{\text{rel.}}$) for the zinc reduction of each cation was determined. The results are listed in

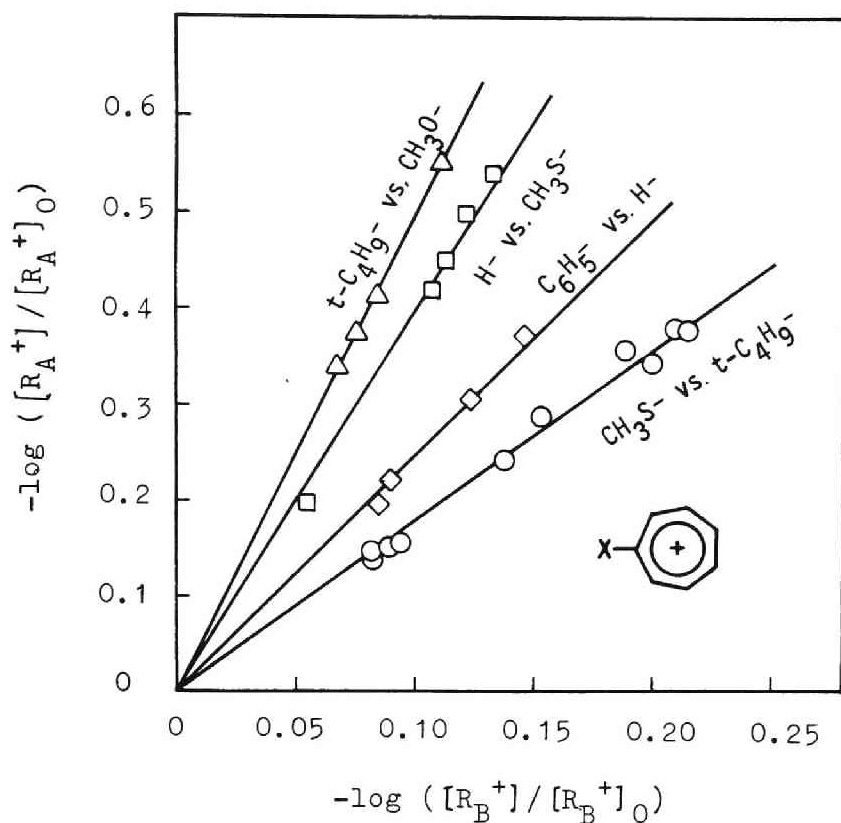


Fig. 2. Plot of $-\log ([R_A^+]/[R_A^+]_0)$ vs. $-\log ([R_B^+]/[R_B^+]_0)$ for the competitive reduction of C_6H_5^- , H^- , CH_3S^- , $t\text{-C}_4\text{H}_9^-$, and $\text{CH}_3\text{O}-\text{C}_7\text{H}_6^+$ with zinc in acetonitrile at 25°C.

Table 3 together with the charge-transfer maxima (vide infra) of the respective cations.

In order to compare the results obtained by the present method ($k_{\text{rel.}}$) with that determined by the homogene-

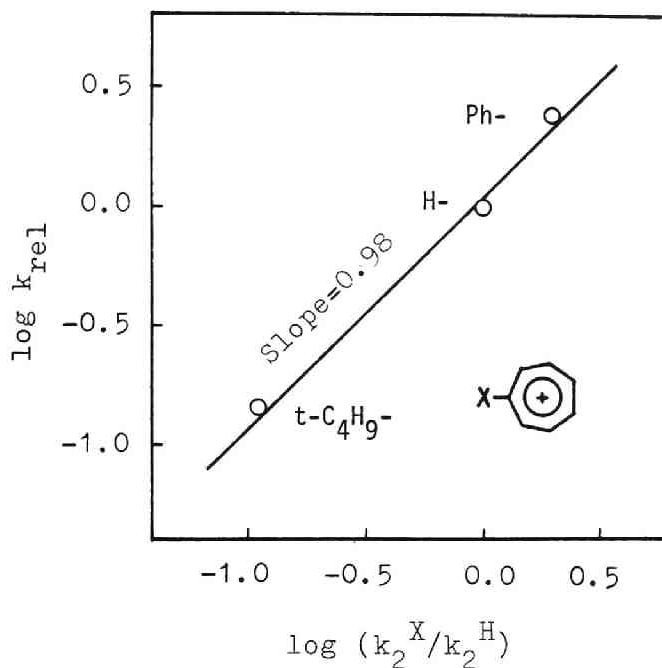


Fig. 3. Plot of $\log k_{rel}$, measured by the competitive reduction vs. $\log (k_2^X/k_2^H)$ determined by Cr(II) reduction.

ous chromous-ion reduction (k_2), $\log k_{rel}$, was plotted against $\log k_2$. A linear correlation with the slope of 0.98 was observed, as is shown in Fig. 3. This result clearly indicates that, in spite of the use of a heterogeneous condition, the present method gives reasonably correct relative values for the reducibility inherent to the carbonium ions.

Table 3. Relative rate constants for the zinc reduction of hetero-atom substituted tropylium ions and absorptions of their charge-transfer spectra

Substituent	$k_{\text{rel.}}^{\text{a)}}$	$\log k_{\text{rel.}}$	C.T. band ^{b)}	
			λ_{max} nm	ν_{max} 10^4 cm^{-1}
$\text{CH}_3\text{O}-$	0.0295	-1.530	480	2.083
$t\text{-C}_4\text{H}_9-$	0.146	-0.836	508	1.969
$\text{CH}_3\text{S}-$	0.255	-0.594	510	1.961
H-	1.00	0.000	540	1.852
C_6H_5-	2.50	0.398	543	1.842
$(\text{C}_6\text{H}_5)_3\text{Si}-$	4.93	0.693	555	1.802
Cl-	11.1	1.044	580	1.724
$\text{CH}_3\text{O}_2\text{C}-$	23.4	1.370	610	1.639
NC-	107	2.030	680	1.471

a) Determined by the competitive reduction in acetonitrile at 25°C.

b) Measured in 1,2-dichloroethane with pyrene as a donor.

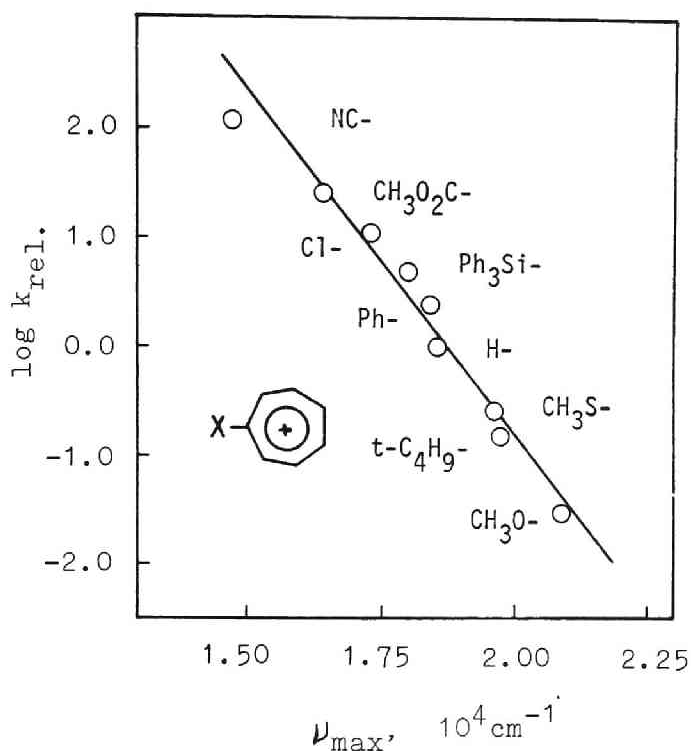


Fig. 4. Plot of $\log k_{rel.}$ vs ν_{max}

The Correlation of $\log k_{rel.}$ with the Charge-Transfer Energy. In order to examine the correlation of the reducibility with the electron-affinity, the values of $\log k_{rel.}$ were plotted against the wave number corresponding to the maximum absorption of the charge-transfer spectrum (ν_{max} , see Table 3) of each substituted tropylium[•] ion with pyrene as a standard electron donor. A good linear correlation was observed, as is seen in Fig. 4. Since, for a given

donor molecule, ν_{\max} for the charge-transfer spectrum of a series of acceptors should correlate with the electron affinity of the acceptors,¹⁵⁾ this correlation (Fig. 4) clearly demonstrates that the reducibility of the carbonium ion is essentially regulated by the electron affinity inherent to the cation itself. Thus, the correlation which holds for the alkyl- and aryl-substituted tropylium ions (Chapters 5 and 6) has been successfully extended to a series of hetero-atom substituted tropylium ions.

The Correlation of $\log k_{\text{rel.}}$ with Hammett's σ_p .
 The variation of the reactivity of substituted tropylium ions obviously reflects the influence of the electronic stabilization or destabilization caused by these substituents. In order to compare the substituent effect with the one observed in the case of substituted phenyltropylium ions (Chapter 6), the values of $\log k_{\text{rel.}}$ were plotted against Hammett's σ_p ¹⁶⁾ (Fig. 5). The one-electron reducibility of the substituted tropylium ion, thus measured, is considered to be an average of the reactivity of the seven individual carbon atoms in the ring toward the reductant. Hence, the use of a single σ_p constant, though it includes both resonance and inductive electronic effects, may not be explicitly applicable. This is perhaps one of the causes for scatters in Fig. 5.¹⁷⁾ Although we can not avoid such a theoretical ambiguity, if we express the sensitivity to the substituent effect by the ρ -value, it would amount to about +4.0. The increase in ρ -value, compared

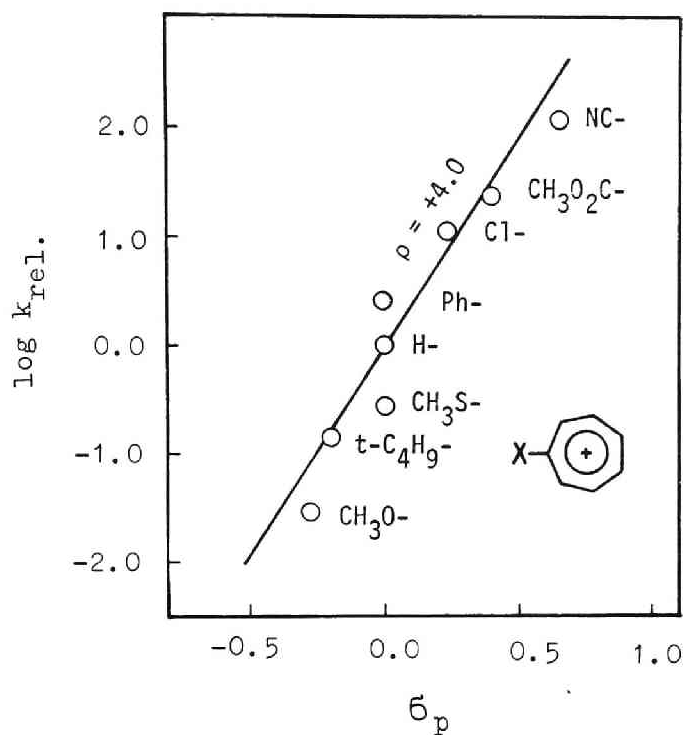


Fig. 5. Plot of $\log k_{rel.}$ vs. σ_p

with that obtained in the case of substituted phenyltropylium system (+1.31), is evidently caused by the direct transmission of the electronic effect of the substituent to the tropylium ring.

Summary

A series of hetero-atom substituted tropylium salts ($X-C_7H_6^+-Y^-$), including three new compounds, have been synthesized. Their relative reactivity in the one-electron reduction with zinc powder has been determined by the use of a competitive-reduction method to give the reactivity sequence: $CH_3O-C_7H_6^+$ ($k_{rel.} = 0.0295$), $t-C_4H_9-C_7H_6^+$ (0.146), $CH_3S-C_7H_6^+$ (0.255), $C_7H_7^+$ (1.00), $C_6H_5-C_7H_6^+$ (2.50), $(C_6H_5)_3Si-C_7H_6^+$ (4.93), $Cl-C_7H_6^+$ (11.1), $CH_3O_2C-C_7H_6^+$ (23.4), $NC-C_7H_6^+$ (107). The values of $\log k_{rel.}$ for $t-C_4H_9-$, $H-$, and $C_6H_5-C_7H_6^+$ ions exhibit a good linear correlation with those of $\log k_2$ in the chromous-ion reduction. A linear correlation also is observed between $\log k_{rel.}$ and the transition energy of the charge-transfer band of the respective cations with pyrene as a donor. A plot of $\log k_{rel.}$ against σ_p (for the ring substituent, X) gives a greater ρ -value (+4.0) than in the case of $X-C_6H_4-C_7H_6^+$ (+1.31), reflecting the influence of the direct substitution to the tropylium ring.

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- 16) The values of σ_p were cited from D. H. McDaniel and H. C. Brown, J. Org. Chem., 23, 420 (1958).
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Fig. 5. This may be a reflection of the fact that the extent of conjugation of the substituent with the seven-membered ring is not changed so much throughout the reaction path from the tropylium ion to the troyl radical, whereas, from the definition, σ_p^+ is applicable to those reactions in which the conjugative interaction of the carbonium-ion center with the substituent arises and develops during the course from the ground state to the intermediate.

Chapter 8 A Kinetic Study on the Reduction of the
Substituted Cyclopropenium Ions with Cr(II)

Introduction

In Chapters 5 and 6 were described the results of kinetic measurements on the chromous-ion reduction of various substituted tropylium ions. It was observed that $\log k_2$ thus obtained has a linear free-energy relationship with the electron affinity, the polarographic half-wave potential, and also with the pK_R^+ values; thus, the $\log k_2$ can be regarded as a relative measure for the electron affinity of the carbonium ions in solution. In order to examine the applicability of this method for stable carbonium ions of the system other than the tropylium ion, the chromous-ion reduction of a series of phenyl and/or n-propyl-substituted cyclopropenium ions was investigated.

In their systematic studies of the syntheses and stability of substituted cyclopropenium ions,¹⁾ Breslow and his co-workers have reported on the polarographic reduction of some p-substituted triphenylcyclopropenium ions^{1c)} and have interpreted the results on the basis of HMO calculations. They have also reported on the zinc reduction of the triphenylcyclopropenium ion to give its dimer,^{1b)} but no kinetic study of the one-electron reduc-

tion for this series of stable carbonium ions seems to have been carried out. In this chapter, the results of the kinetic measurements and their correlation with the electron affinities and pK_R^+ 's of the cyclopropenium ions will be discussed in comparison with the results previously obtained for a series of substituted tropylium ions.

Experimental²⁾

Materials. All the reagents employed were of a reagent- - grade quality except when otherwise noted. Acetonitrile and ethyl acetate were refluxed and distilled over phosphorous pentoxide; acetonitrile, bp, 81.0-81.3°C; ethyl acetate, bp, 77.0-77.5°C. Ethyl ether was dried over sodium metal.

Triphenylcyclopropenium fluoroborate ($Ia \cdot BF_4^-$) was prepared from triphenylcyclopropenyl methyl ether^{1a)} as follows. Into a solution of 0.964 g (3.23 mmol) of triphenylcyclopropenyl methyl ether in 15 ml of methanol, was added 1.0 ml of 42% aqueous fluoroboric acid. The white precipitates which were immediately formed were collected, washed with dry ethyl ether, and dried under reduced pressure to give 0.925 g (2.62 mmol) of $Ia \cdot BF_4^-$ as white crystals; 81.1% yield; mp 308-310°C (dec); $\lambda_{max}^{2.9 M HCl}$ 259 nm (ϵ , 18100), 309 nm (64100), 324 nm (54500).

Diphenyl-n-propylcyclopropenium fluoroborate ($Ib \cdot BF_4^-$)

was prepared following the method of Breslow et al.;^{1f)}
mp 175-177°C (dec) (lit,^{1f)} mp 179°C (dec)); $\lambda_{\text{max}}^{2.9 \text{ M HCl}}$
246 nm (ϵ , 15700), 293 nm (33600), 307 nm (34400) (lit,^{1f)}
 $\lambda_{\text{max}}^{1 \text{ M HCl}-23\% \text{ EtOH}}$ 292 nm (ϵ , 32000), 305 nm (33000)).

Di-n-propylphenylcyclopropenium perchlorate ($\text{Ic} \cdot \text{ClO}_4^-$)
was prepared from the di-n-propylcyclopropenium ion^{1f)} as
follows. To a suspension of 1.503 g (6.74 mmol) of di-n-
propylcyclopropenium perchlorate in 10 ml of dry ethyl
ether, was slowly added 20 ml of a 1 M ethereal solution
of phenyllithium (20 mmol) with vigorous stirring at -78°C.
The stirring was continued for 1 hr at -78°C and then for
an additional hour at room temperature. To the reaction
mixture was then added 30 ml of 1 M HCl, and the aqueous
layer was extracted with three 40-ml portions of ethyl
ether. The combined ethereal solution was washed with
10% NaCl and dried over MgSO_4 . The solvent was removed
in vacuo to give 1.60 g of a brownish oil which was sup-
posed to be crude 1,2-di-n-propyl-3-phenyl-1-cyclopropene.
To this oil was then added a solution of 0.769 g (2.25
mmol) of triphenylmethyl perchlorate³⁾ in 24 ml of aceto-
nitrile, and the whole mixture was let stand for 30 min
at room temperature. The solvent was evaporated under
reduced pressure. Then, 10 ml of ethyl acetate and 100
ml of dry ethyl ether were added to the dark-brown resi-
dual oil to cause the formation of white precipitates.
The precipitates were collected, washed with dry ethyl
ether, and dried in vacuo to give 0.537 g (1.89 mmol) of

$\text{Ic} \cdot \text{ClO}_4^-$ as white crystals, which can be recrystallized from chloroform-ethyl ether; 80.0% yield, based on triphenylmethyl perchlorate; mp $157.5\text{--}158.5^\circ\text{C}$ (dec); $\lambda_{\text{max}}^{2.9 \text{ M HCl}}$ 262 nm (ϵ , 26400); NMR (100 MHz), τ_{CDCl_3} 2.89 (d, 2H, ortho-protons), 3.10 (t, 1H, para-proton), 3.25 (t, 2H, meta-protons), 7.08 (t, 4H, α -methylene protons), 8.23 (sext, 4H, β -methylene protons), 9.07 (t, 6H, methyl protons); $\nu_{\text{max}}^{\text{KBr}}$ 695, 780, 1095, 1440, 1460 (sh), 1500, 1600, 2900, 3000cm^{-1} .

Found: C, 60.26; H, 6.49%. Calcd for $\text{C}_{15}\text{H}_{19}\text{ClO}_4$: C, 60.30; H, 6.41%.

Tri-n-propylcyclopropenium perchlorate ($\text{Id} \cdot \text{ClO}_4^-$)
was prepared according to the method of Breslow et al.,^{1f)}
mp $183.5\text{--}185^\circ\text{C}$ (lit.,^{1f)} $184\text{--}185^\circ\text{C}$)

A solution of chromous chloride in 2.9 M HCl was prepared as described in previous chapters.

One-Electron Reduction of the Cyclopropenium Ions.
Reduction of Ia with Cr(II). In a 200-ml, four-necked flask equipped with a mechanical stirrer, a serum rubber cap, and a nitrogen inlet and outlet, there was charged a solution of 0.105 g (0.295 mmol) of $\text{Ia} \cdot \text{BF}_4^-$ in 100 ml of 2.9 M HCl. To this solution was then added 20 ml of 1.17 M solution of chromous chloride in 2.9 M HCl by the use of a hypodermic syringe. The solution was stirred at 25°C for 21 hr under an atmosphere of nitrogen, and then the organic product was extracted with four 100-ml portions of n-hexane, washed with 10% NaCl, and dried over

MgSO₄. The solvent was subsequently removed in vacuo to give 0.0758 g (0.142 mmol) of bis(1,2,3-triphenyl-2-cyclopropen-1-yl) (II) as white crystals; 96.2% yield; mp 223-225°C (lit.,^{1c}) mp 225-226°C); NMR (60 MHz), τ_{CDCl_3} 2.65 (br.s, phenyl protons).

Reduction of Ib with Cr(II). In the same manner, the reduction of 0.131 g (0.409 mmol) of Ib·BF₄⁻ with 46 mmol of chromous chloride was carried out in 160 ml of 2.9 M HCl at 75°C for 22 hr under a nitrogen atmosphere. The reaction mixture was worked up in the same way to give 0.0927 g of a crude product, which was then purified by the use of preparative thin-layer chromatography over silica-gel (Merck, Kieselgel PF₂₅₄), with n-hexane-benzene (3:1) as the solvent, to give 0.0781 g (0.168 mmol) of bis(1,2-diphenyl-3-n-propyl-2-cyclopropen-1-yl) (III) as white crystals; 82.1% yield; mp 152-159°C (with rapid resolidification⁴); $\lambda_{\text{max}}^{\text{EtOH}}$ 267 nm (ϵ , 16300); $\nu_{\text{max}}^{\text{KBr}}$ 690, 700, 760, 800, 1025, 1090, 1265, 1440, 1495, 1600, 1850, 3000 cm⁻¹; NMR (100 MHz), τ_{CCl_4} 2.78, 2.97 (m and s, 20H, phenyl), 7.30 (t, 4H, α -methylene), 8.30 (sext, 4H, β -methylene), 8.99 (t, 6H, methyl).

Reduction of Ic with Zn and with Cr(II). In a similar manner, 2.0 g (30 mg-atom) of zinc powder was added to a solution of 0.201 g (0.670 mmol) of Ic·ClO₄⁻ in 85 ml of 0.1 M HCl; the mixture was then magnetically stirred at 20°C for 5 hr under an atmosphere of nitrogen. Then the unchanged zinc was filtered off and washed with four 50-ml

portions of ethyl ether. The aqueous solution was extracted with three 70-ml portions of ethyl ether, and the combined ethereal solution was washed with 10% NaCl, dried over MgSO_4 , and evaporated to give 0.130 g of a partially-solidified yellowish oil, which gave three main spots (R_f , 0.23, 0.4-0.5, and 0.67) on a silica-gel thin-layer plate, with n-hexane-benzene (9:1) as the solvent. By the use of preparative thin-layer chromatography, a component with R_f 0.67 was isolated as 0.0512 g of a colorless oil and was identified as bis(1,2-di-n-propyl-3-phenyl-2-cyclopropen-1-yl) (IV); 0.129 mmol; 38.5% yield; $\nu_{\text{max}}^{\text{CCl}_4}$ 695, 1380, 1440, 1460, 1490, 1600, 1830, 2900, 2970, 3000 cm^{-1} ; NMR (60 MHz), $\tau_{\text{CCl}_4}^{5)}$ 2.70 (s, ~10H, phenyl), 7.80 (m, 8H, α -methylene), (m, 8H, β -methylene), 9.00 (m, ~12H, methyl). In the same way, a component with R_f 0.23 was isolated as 0.0527 g of white crystals and was identified as bis(2,3-di-n-propyl-1-phenyl-2-cyclopropen-1-yl) (V); 0.133 mmol; 39.7% yield; mp 26.0-28.0°C; $\lambda_{\text{max}}^{\text{EtOH}}$ 240 nm (ϵ , 9400), 273 nm (sh) (1100), 280 nm (763); $\nu_{\text{max}}^{\text{CCl}_4}$ 700, 1380, 1440, 1450, 1460, 1490, 1600, 1870, 2900, 2970, 3000 cm^{-1} ; NMR (100 MHz), $\tau_{\text{CCl}_4}^{6)}$ 3.00 (s, 10H, phenyl), 7.56 (t, 8H, α -methylene), 8.43 (sext, 8H, β -methylene), 9.04 (t, 12H, methyl). On the other hand, the component with R_f 0.4-0.5 gave 0.0202 g of a pale yellow oil, which exhibited an infrared spectrum quite similar to those of IV and V, though its structure was not fully identified.

For the purpose of comparing the reaction products, a

reduction of Ic with Cr(II) was conducted in the following way. To a solution of 0.0164 g (0.0548 mmol) of $\text{Ic} \cdot \text{ClO}_4^-$ in 8.0 ml of 2.9 M HCl placed in a 20-ml ampoule we added 8.0 ml of a 1.3 M solution of chromous chloride in 2.9 M HCl by the use of a hypodermic syringe under a stream of nitrogen. The ampoule was immediately sealed under nitrogen and immersed in an oil bath thermostated at 125°C . After 20 hr the organic products were extracted with three 20-ml portions of ethyl ether, washed with 10% NaCl, and dried over MgSO_4 . The evaporation of the ethereal solution under reduced pressure gave 0.0112 g of a partially-solidified, yellowish oil, which was found to contain the same products in the same composition as in the case of the zinc reduction of Ic described above, on the basis of an analysis with thin-layer chromatography.

Attempted Reduction of Id with Cr(II). The reaction of 0.0193 g (0.0730 mmol) of $\text{Id} \cdot \text{ClO}_4^-$ with the chromous ion (2.64 mg-ion) in 4.0 ml of 2.9 M HCl at 125°C was attempted in an ampoule in the same way as has been described above. After 48 hr, the solution was worked up in the same way to give 0.0031 g of an unidentified oil. This was shown to contain the same components as in the case of the control experiments in which the cation, Id, alone was kept at 125°C under the same conditions. The acidic aqueous layer was made alkaline with 10% NaOH, and the turbid solution which resulted was worked up in the usual way to give 0.0093 g of a colorless oil which was

tentatively identified as 1,2,3-tri-n-propyl-2-propen-1-one on the basis of its infrared spectrum and also by analogy with the alkaline ring opening of Ia giving 1,2,3-triphenyl-2-propen-1-one;^{1a)} 0.056 mmol; 77% yield; $\nu_{\text{max}}^{\text{CCl}_4}$ 1380, 1460, 1665, 2900, 2980 cm^{-1} .

Kinetic Measurements. The rates of the reduction of Ia and of Ib were measured in the following way. A solution of a weighed amount of the cyclopropenium salt in 40 ml of 2.9 M HCl was charged in a 100-ml, four-necked flask equipped with a mechanical stirrer, a serum rubber cap, and a nitrogen inlet and outlet. The solution was bubbled with nitrogen for 10 min, while the reaction flask was placed in a thermostated bath. To this solution we then added a known amount (4.0-12.0 ml) of a 1.30 M solution of chromous chloride in 2.9 M HCl by the use of hypodermic syringe, and the solution was stirred under an atmosphere of nitrogen. At appropriate time intervals, 2.00-ml aliquots were sampled out by the use of a hypodermic syringe, extracted with three 5-ml portions of n-hexane, and diluted to a 100-fold volume with 2.9 M HCl. The amount of the unchanged cyclopropenium ion was analyzed on the diluted solution by means of ultraviolet spectrophotometry, using 308 nm (ϵ , 52800) as the characteristic band for Ia and 307 nm (ϵ , 34400) for Ib. The rate constants were calculated from the first-order rate equation and treated as has been described in text. The initial concentrations of the cyclopropenium ion and of the chromous

ion were determined by ultraviolet spectroscopy and by iodometry respectively.

The kinetic measurements of the reduction of Ic were conducted by the use of the sealed-ampoule technique. To 1.0-ml portions of the solution of Ic in 2.9 M HCl placed in ampoules we added 1.0-ml portions of a 1.30 M solution of chromous chloride in 2.9 M HCl under a stream of nitrogen. The ampoules were immediately sealed and immersed in a thermostated bath. At appropriate time intervals the ampoules were opened and the amount of the unchanged cyclopropenium ion was determined spectrophotometrically, using 262 nm (ϵ , 26400) as the characteristic band; the results were then treated according to the first-order rate equation.

As has been mentioned in the previous section, the cation, Id, was not appreciably reduced with the chromous ion and was recovered in a 77% yield under the given reaction conditions. Even when it is assumed that the unrecovered amount corresponds to the reduction products which might have been decomposed to unidentified materials, a 77% recovery after the reaction time of 48 hr in the presence of 0.66 M of the chromous chloride gives the value of $2.3 \times 10^{-6} \text{ M}^{-1} \cdot \text{sec}^{-1}$ for the upper limit of the apparent second-order rate constant; the real rate constant must be much smaller than this value.

The Solubility of $\text{Ia} \cdot \text{BF}_4^-$ in Aqueous HCl with and without NaCl. In 10-ml test tubes with ground glass

stoppers we placed various mixtures of 0.010-g portions of $\text{Ia} \cdot \text{BF}_4^-$ with 2.0-ml portions either aqueous HCl or aqueous HCl containing NaCl; the mixtures were shaken vigorously for 50 hr at 15-21°C. Each mixture was then filtered, and an amount of Ia dissolved in the filtrate was determined by ultraviolet spectroscopy.

Measurements of the Charge-Transfer Bands with Pyrene. 1,2-Dichloroethane solutions of the cyclopropenium ion (3×10^{-3} g.ion/l) and of pyrene (2×10^{-1} M) were mixed in the dark⁷⁾ to give a slightly orange-colored, yellowish solution, and its visible spectrum was immediately recorded. In the cases of Ia and Ib, a widely-absorbing shoulder, which was not observed in the spectrum of either single component, appeared at the longer wavelength. These new absorptions were supposed to be due to the formation of charge-transfer complexes; the values of the wavelength corresponding to the midpoint of the new band are listed in Table 3 (see Results and Discussion).

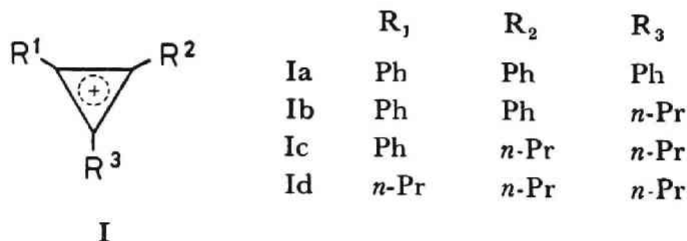
On the other hand, only the end absorption was observed in the region of wavelengths longer than pyrene in the cases of Ic and Id.

Determination of pK_R^+ 's. The pK_R^+ 's of Ia, Ib, and Ic were determined in 23% aqueous ethanol at 25°C, as has been described by Breslow and Chang,^{1d)} by the use of the spectrophotometric method. Because the characteristic bands of the cations were found to decrease during the measurements for Ib and Ic, the absorbance, which was

extrapolated to the time of the dissolution of the cations, was plotted against pH to give classical titration curves, whose inflection points were taken as pK_R^+ 's. The pH's were read on a Horiba model H pH meter calibrated with standard buffers before use.

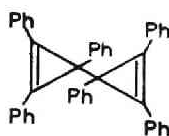
Results and Discussion

One-Electron Reduction of the Cyclopropenium Ions
(Product Study). A series of cyclopropenium ions substituted with phenyl and/or n-propyl groups (Ia-d) was prepared according to the method of Breslow et al.,^{1d,f)} except for Ic, which is a new compound and which was synthesized by analogy with the synthesis of Id.^{1f)}

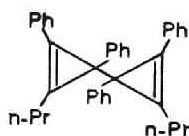


The reduction of the cyclopropenium ions, Ia-d, with the chromous ion was carried out in 10% HCl (2.9 M) under an atmosphere of nitrogen at an appropriate temperature (Ia : 25°C, Ib : 75°C, Ic, d : 125°C).⁸⁾ Ia, Ib, and Ic were found to be reduced with Cr(II) to give dimers in almost quantitative yields, as in the case of the zinc

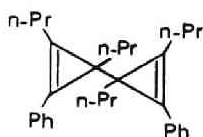
reduction of Ia.^{1b)} The reduction products of Ia and Ib were purified by thin-layer chromatography and were identified as bis(1,2,3-triphenyl-2-cyclopropen-1-yl) (II) and bis(1,2-diphenyl-3-n-propyl-2-cyclopropen-1-yl) (III) respectively. On the other hand, the reduction of Ic with Cr(II) was too slow to give the reduction product in an amount sufficient for the structural analysis. Therefore, Ic was reduced with zinc powder for the purposes of the product analysis. Preparative thin-layer chromatography showed that the product was the same as in the case of the chromous-ion reduction and that it contained bis(1,2-di-n-propyl-3-phenyl-2-cyclopropen-1-yl) (IV) and bis(2,3-di-n-propyl-1-phenyl-2-cyclopropen-1-yl) (V) in almost equal amounts. The cation, Id, was quite inert to the chromous-ion reduction and gave a trace of an unidentified oil only, after a reaction time of 48 hr at 125°C.



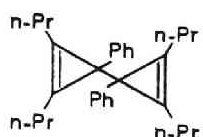
(II)



(III)



(IV)



(V)

Kinetic Measurements for the Reduction of the Triphenylcyclopropenium Ion with Cr(II). The Effect of the Added Anion. The reactions of the triphenylcyclopropenium ion (Ia) with a large excess of Cr(II) were conducted in 2.9 M HCl under an atmosphere of nitrogen, and the decrease in the unchanged carbonium ion was followed by ultraviolet spectroscopy; in all cases, good first-order behavior was observed. The first-order rate constants thus obtained

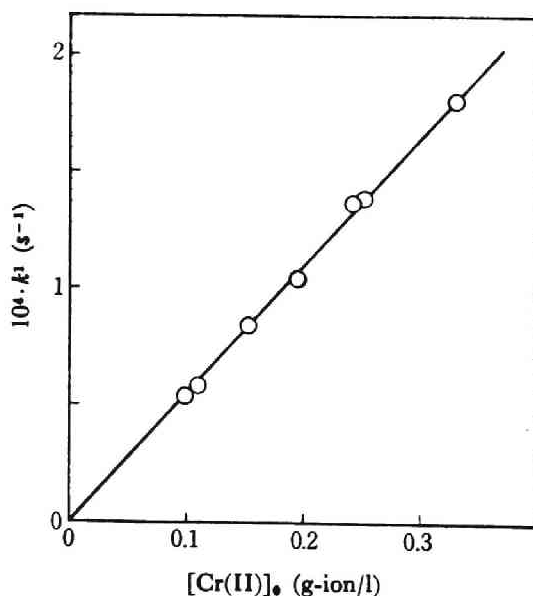


Fig. 1. Dependence of the first-order rate constant (k_1) for the chromous-ion reduction of Ia on the initial concentration of Cr(II).

[Ia]₀: 3.0×10^{-3} g-ion/l, Temperature: 30.0 °C, Solvent: 2.9 M HCl

were proportional to the initial concentrations of Cr(II), as is shown in Fig. 1 for the reactions at 30°C, indicating that the overall reaction rate can be expressed by the ordinary second-order rate equation: $\text{rate} = k_2[\text{Ia}] \cdot [\text{Cr(II)}]$. The second-order rate constants determined in this way at various temperatures are listed in Table 1. From the Arrhenius plot, the values of an activation energy and an activation entropy were estimated to be 13.9 kcal/mol and -7.1 e.u. at 25°C.

In a previous mechanistic study, described in Chapter 4, the chloride ion added either as HCl or NaCl was shown to accelerate the chromous-ion reduction of the tropylium ion, possibly because of the effectiveness of the chloride ion in forming an electron-transfer bridge between the two

TABLE 1. RATES OF THE CHROMOUS-ION REDUCTION OF THE TRIPHENYLCYCLOPROPENIUM ION (Ia) IN 2.9 M HCl

Temp. °C	Initial concn		$10^4 \cdot k_2$ l/g-ion·s	Number of measure- ments
	[Ia] ₀ g-ion/l	[Cr(II)] ₀ g-ion/l		
25.0	6.87×10^{-4}	0.139	3.0 ± 0.2	5
30.0	2.99×10^{-4}	0.198	5.4 ± 0.4	7
35.0	2.75×10^{-4}	0.158	8.0 ± 0.5	4
45.0	2.77×10^{-4}	0.141	15.2 ± 0.7	3
50.0	3.02×10^{-4}	0.130	22.2 ± 1.9	4

reagents. It was observed that this rate-increasing effect gradually reaches its maximum in the anion concentration range of 3-4 g·ion/l; consequently, the reaction was expected to proceed completely by way of the chloride-ion bridging in this concentration range. Therefore, 10% HCl (2.9 M) was chosen as the standard solvent for the previous study on the reduction of the substituted tropylium ions (Chapters 5 and 6) and also for the present study.

However, the effects of the added HCl and NaCl⁹⁾ on the reduction rate of the triphenylcyclopropenium ion characteristically showed different tendencies from each other, as is shown in Fig. 2; addition of NaCl brings about a remarkable rate-enhancement, whereas the increase in the HCl concentration results in a initial rate-enhancement, followed by a slight rate-retarding effect. On the other hand, the effects of the concentration of added HCl and/or NaCl on the solubility (saturation concentration) of the carbonium ion (Fig. 3) exhibit a reversal of the tendency of the reduction rate (Fig. 2). From a comparison of the tendencies shown in Figs. 2 and 3, it may be supposed that undissociated HCl molecules (or $[H-Cl-H]^+$ ions), which are predominant at higher HCl concentrations, strongly stabilize or solvate the carbonium ion, thus increasing the solubility but preventing an attack by Cr(II), whereas the free Cl^- ions from the added NaCl suppress the solubility but facilitate the chromous-ion reduction by means of a ready formation of a Cl^- bridge between the two reagents.

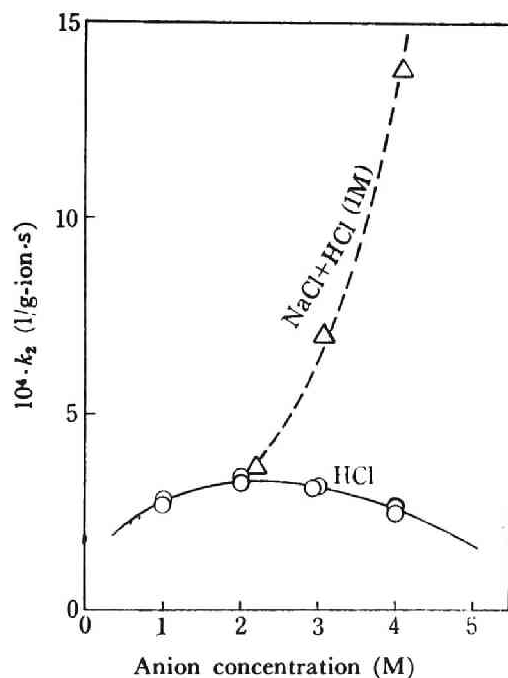


Fig. 2. The effect of an added anion on the reduction rate of Ia with Cr(II) at 25 °C.

○: Effect of HCl concentration. ($[Ia]_0 = 1.6 \times 10^{-3}$ g-ion/l, $[Cr(II)]_0 = 0.14$ g-ion/l)

△: Effect of the concentration of NaCl added to 1 M HCl. ($[Ia]_0 = 7.8 \times 10^{-4}$ g-ion/l, $[Cr(II)]_0 = 0.14$ g-ion/l)

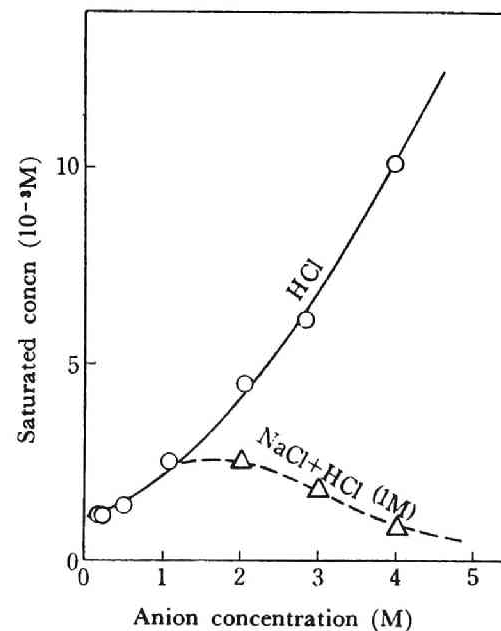


Fig. 3. The effect of an added anion on the saturated concentration of Ia in aqueous HCl solution.

○: Effect of HCl concentration.

△: Effect of the concentration of NaCl added to 1 M HCl.

Kinetic Measurements for the Reduction of the Cyclopropenium Ions with Cr(II). The second-order rate constants for the chromous-ion reduction of Ia, Ib, Ic, and Id are listed in Table 2. It is apparent that the substitution of the n-propyl group for the phenyl group brings about a great suppression in the reactivity of the cyclopropenium ions. This is in accord with the increase in the stability of the cyclopropenium ion by the substitution of the n-propyl group, as has already been reported;^{1f)} this is the same trend as is seen in the reduction of the substituted tropylium ions, although the latter reaction is much more rapid as has been described in Chapter 5.

Correlation of the Reducibility with the Electron Affinity and with pK_R^+ . Several examples of charge-transfer (C.T.) interactions between carbonium ions and some aromatic hydrocarbons have been reported,¹⁰⁾ and the relationship between the C. T. transition energy and the electron affinity of the carbonium ion has been discussed.^{10c,e,f)} We also observed the C. T. band when the cyclopropenium ions, Ia and Ib, were added to a 1,2-dichloroethane solution of pyrene. The values of the electron affinity were estimated from the C. T. transition energies by a method previously reported by Feldman and Winstein,^{10e)} and the correlation of $\log k_2$ with the electron affinity was examined together with the cases of substituted tropylium ions. From the results shown in Table 3 and Fig. 4, it may be seen that the linear relationship observed between

TABLE 2. RATES OF THE CHROMOUS-ION REDUCTION OF THE CYCLOPROPENIUM IONS (Ia-d) IN 2.9 M HCl

Cyclopropenium ion	Temp. °C	Initial concn		k_2 l/g-ion·s	ΔE_a kcal/mol
		$10^3[I]_0$ g-ion/l	$10[Cr(II)]_0$ g-ion/l		
Ia	25.0	1.51	1.31	3.01×10^{-4}	13.9
Ib	75.0	2.30	2.81	4.85×10^{-4}	—
	50.0	2.30	2.81	4.45×10^{-5}	—
	25.0	—	—	2.72×10^{-6} a)	21.3
	25.0	—	—	2.78×10^{-9} a)	20.2
Ic	125.0	2.31	6.50	1.53×10^{-5}	—
	100.0	2.31	6.50	2.75×10^{-6}	—
	25.0	—	—	2.78×10^{-9} a)	20.2
Id	125.0	3.77	6.68	$< 10^{-6}$ c)	—
	25.0	—	—	$< 10^{-11}$ b)	—

a) Extrapolated from the data at elevated temperatures.

b) Estimated by the assumption that the activation energy is the same as in the case of Ic.

c) An estimated value (see Experimental).

TABLE 3. RESULTS OF THE MEASUREMENTS OF REDUCTION RATES, CHARGE-TRANSFER BANDS,
AND pK_R 'S OF THE STABLE CARBONIUM IONS

Carbonium ion	log $k_2^{a)}$	C. T. band ^{b)}		$pK_R^{d)}$	
		$\lambda_{max}, m\mu$	$E_{aff.}^{c)}, eV$	Obs'd	Lit. ^{3f)}
Cyclopropenium Ion					
Ia	-3.51	~420	~5.71	2.6	2.8
Ib	-5.57	~415	~5.68	4.0	3.8
Ic	-8.56	—	—	5.6	—
Id	< -11	—	—	—	7.2 ^{e)}
Tropylium ion ^{f)}					
Trityl	2.75	550—560	6.27—6.30	3.6	
Phenyl	2.16	543	6.25	4.1	
Unsubst'd	1.87	540	6.24	4.3	
Methyl	1.05	513	6.13	—	
Ethyl	1.01	512	6.13	—	
Isopropyl	0.91	505	6.10	—	
<i>t</i> -Butyl	0.90	508	6.11	5.0	

a) The logarithmic value of the rate constant for the chromion reduction of the respective carbonium ion. b) Measured in 1,2-dichloroethane with pyrene as a donor. c) Estimated by the method reported by Feldman and Winstein from the relation, $E_{CT} = [I_p]_{Donor} - [E_{Aff}]_{Acceptor} + Const.$ (Ref. 6c) d) Measured spectrophotometrically in 23% ethanol. e) Determined by potentiometric titration in 50% aq. acetonitrile. f) Data from Chapter 5.

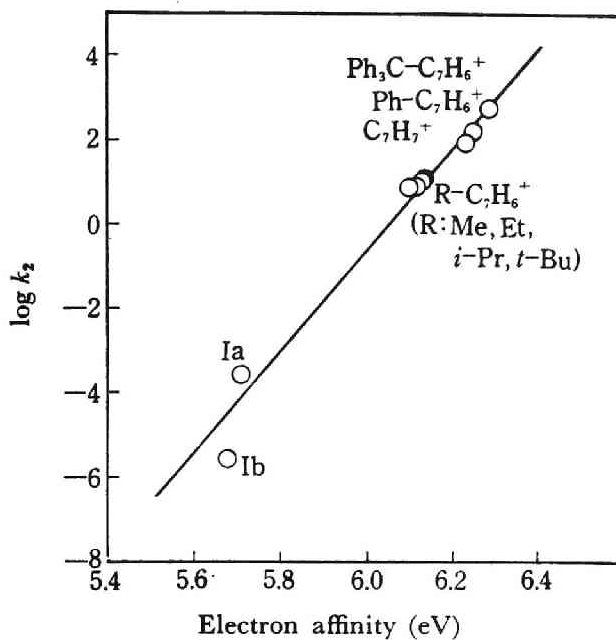


Fig. 4. The correlation of $\log k_2$ with electron affinities of the carbonium ions.

the chromous-ion reducibility and the electron affinity of the substituted tropylium ion extends also to the cyclopropenium system suggesting that the reduction of the tropylium and cyclopropenium ions proceeds by a similar mechanism, with the electron-transfer step as the rate-determining one.¹¹⁾ Thus, it seems that the value of $\log k_2$ for the chromous-ion reduction may be regarded as a chemical criterion for the electron affinity of the stable carbonium ions in solution.

A plot of $\log k_2$ against the pK_{R^+} values measured spectrophotometrically in 23% ethanol also exhibits a good linear relationship, as is shown in Fig. 5. The straight line thus obtained apparently lies parallel with that obtained in the case of the substituted tropylium ions. From the definition, pK_{R^+} value is represented as the difference between $\log k_b$ and $\log k_f$, where k_f denotes the rate constant for the hydrolysis of the carbonium ion, and k_b , that for the reverse reaction.

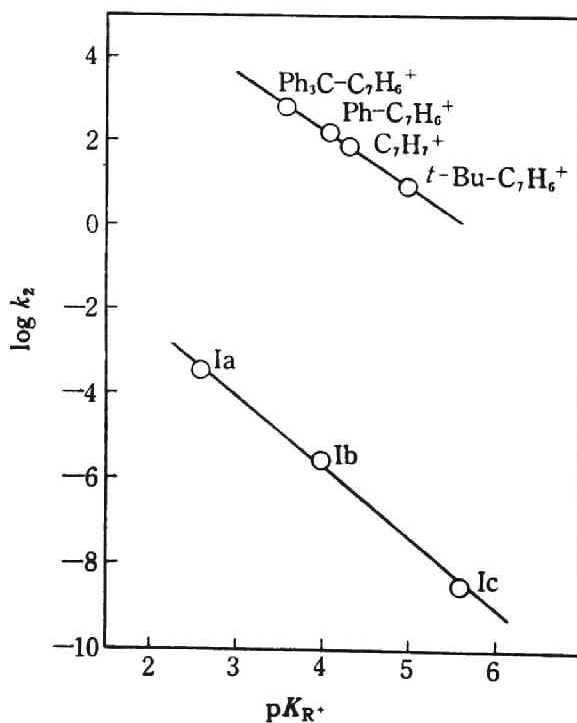
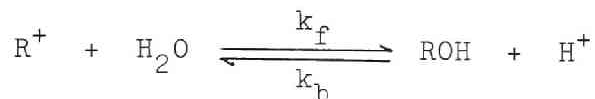


Fig. 5. The correlation of $\log k_2$ with pK_{R^+} .



It may be supposed that $\log k_2$ (a measure for the electron affinity) might linearly correlate with $\log k_f$ (a measure for the electrophilicity of R^+), but not with $\log k_b$ (a measure for the nucleophilicity of ROH). This may be one of the reasons for the separation of the plot of $\log k_2$ vs. pK_R^+ into two lines (in Fig. 5); further relevant studies remain to be done before we can account for these tendencies in more details.

Summary

The one-electron reduction of a series of phenyl- and/or n-propyl-substituted cyclopropenium ions with Cr(II) has been carried out in a 10% HCl solution. The reduction of triphenylcyclopropenium (Ia), diphenyl-n-propylcyclopropenium (Ib), and phenyl-di-n-propylcyclopropenium (Ic) ions quantitatively gives dimers of the respective cyclopropenyl radicals, i.e., the bis(cyclopropenyl) derivatives, whereas the tri-n-propylcyclopropenium ion (Id) is quite unreactive. A kinetic study has shown that the reactivity of these stable carbonium ions toward the one-electron reductant (Cr(II)) is lowered with a decrease in the number of the phenyl substituent: $k_2^{25^\circ C} = 3.0 \times 10^{-4} \text{ l/g-}$

ion·sec for Ia, 2.7×10^{-6} 1/g-ion·sec for Ib, 2.8×10^{-9} 1/g-ion·sec for Ic, and $<10^{-11}$ 1/g-ion·sec for Id. The added NaCl was found to accelerate the reduction rate of Ia, whereas the added HCl showed a initial rate-enhancement effect, followed by a slight rate-retarding effect. A plot of $\log k_2$ against the electron affinities of the respective cations, estimated from the transition energies of the charge-transfer bands for Ia, b with pyrene, has been found to fit a linear correlation previously obtained for a series of tropylium ions. The values of $\log k_2$ also exhibit a linear free-energy relationship with the pK_R of these cations.

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- 2) The melting points and boiling points are uncorrected. The microanalyses were performed by the Microanalytical Center, Kyoto University, Kyoto. The infrared and ultraviolet spectra were taken on Shimadzu models

IR-27 and UV-50M spectrometers respectively. The 60 MHz and 100 MHz NMR spectra were obtained with a JOEL model JNM-3H-60 spectrometer and a Varian model HA-100D spectrometer respectively, with tetramethylsilane as the internal standard.

- 3) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, J. Org. Chem., 25, 1442 (1960).
- 4) This resolidification may indicate a thermal rearrangement of III to a tetraphenyldi-n-propylbenzene derivative, as was observed in the case of II,^{1b)} but no further examination on the rearranged product was attempted.
- 5) The chemical shift of the phenyl protons shows that the phenyl group is attached to an olefinic carbon; also the complex multiplicity of the signals of propyl groups seems to indicate the presence of two types of propyl groups with different magnetic environments.
- 6) The phenyl group has been shown to be attached to a saturated carbon, while the propyl group is supposed to be of only one type, for reasons previously presented.⁵⁾
- 7) It was observed that the exposure of the mixed solution to room light caused the appearance of new absorption bands at 430 and at 455 nm which seemed to be due to some photochemical reaction products, but the nature of the reaction was not investigated further.
- 8) A control experiment showed that either the carbonium ion or the chromous ion was stable enough at the respective temperature.

- 9) Because of the poor solubility of the triphenylcyclopropenium ion in a dilute HCl solution ($<1M$), the effect of HCl in concentrations of less than $1M$ was not examined.
- 10) a) M. Feldman and S. Winstein, J. Amer. Chem. Soc., 83, 3338 (1961). b) M. Nepras and R. Zahradnik, Collection Czech. Chem. Commun., 29, 1545 (1964). c) M. Feldman and B. G. Graves, J. Phys. Chem., 70, 955 (1966). d) S. N. Bhat and C. N. R. Rao, J. Chem. Phys., 47, 1863 (1967). e) M. Feldman and S. Winstein, Theor. Chim. Acta, 10, 86 (1968). f) H. J. Dauben, Jr., and J. D. Wilson, Chem. Commun., 1968, 1629. g) T. G. Beaumont and K. M. C. Davis, J. Chem. Soc. (B), 1968, 1010.
- 11) In view of the effects of the added HCl and NaCl, the reduction of cyclopropenium ions in $2.9 M$ HCl may not proceed completely by way of Cl^- bridging, and thus the values of k_2 measured in $2.9 M$ HCl may be rather smaller than those for the complete Cl^- bridging. However, this uncertainty is assumed to be within one unit in the $\log k_2$ scale; therefore, the $\log k_2 - E_{Aff}$ plot (Fig. 4) may be regarded as still linear, even if we take this uncertainty into consideration.

Chapter 9 The Homolytic Dissociation of 7-Triphenylmethyl- -
1,3,5-cycloheptatriene in m-Xylene

Introduction

From the results described in Chapter 2 was presumed the greater reducibility of the triphenylmethyl cation than the tropylium ion, which is in accord with the values reported of the polarographic half-wave potentials and of the ionization potentials of the corresponding radicals and also with the results of HMO calculations. An attempt to confirm this reducibility relationship between the cations of different structural systems was made, applying the competitive-reduction method described in the preceding chapter; from the reaction products obtained in this experiment was isolated a cross-coupling product of the radicals derived from the respective cation, namely 7-triphenylmethyl-1,3,5-cycloheptatriene. This chapter describes a characteristic behavior, i.e., a ready homolytic dissociation, observed with regard to this compound.

The enthalpy of the dissociation of bitropyl (bis-2,4,6-cycloheptatrien-1-yl) into the troyl (cycloheptatrienyl) radicals has recently been evaluated to be 35 ± 1 kcal/mol using ESR spectroscopy,¹⁾ whereas that of "hexaphenylethane," whose structure has been proved to be

1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene (I),²⁾ into the trityl (triphenylmethyl) radicals is known to be only about 11.5 kcal/mol.³⁾ When these two values are available, it is of considerable interest to know the value of the dissociation energy of 7-trityltropilidene (7-triphenylmethyl-1,3,5-cycloheptatriene), a coupling product of the trityl and tropylium radicals. Thus, the measurement of the degree of the dissociation by means of ESR spectroscopy was carried out in order to evaluate the enthalpy of the dissociation of this compound.

Experimental⁴⁾

Materials. All the reagents employed were of a reagent-grade quality. Acetonitrile was refluxed and distilled over phosphorus pentoxide; bp 80.8-81.2°C. m-Xylene was dried over sodium and fractionally distilled; bp 138.5-139.5°C.

Tropylium fluoroborate was prepared from tropilidene according to the method of Conrow.⁵⁾ Triphenylmethyl fluoroborate was prepared from triphenylcarbinol according to the method of Dauben, et al.⁶⁾

Competitive Reduction of the Triphenylmethyl Cation and the Tropylium Ion with Zinc Powder. Into a magnetically stirred solution of 1.656 g (5.02 mmol) of triphenylmethyl fluoroborate and 0.891 g (5.00 mmol) of tropylium

fluoroborate in 50.0 ml of acetonitrile, which had been kept at -9°C in a NaCl-ice bath, there was added 0.261 g (4.00 mg-atom) of zinc powder in a stream of nitrogen. The mixture was stirred for 5 min under a nitrogen atmosphere; the initial deep-orange color of the solution turned to light yellow and, instead, a formation of white precipitates, presumably the "hexaphenylethane", was observed. To this mixture were then added 30 ml of water and 40 ml of ethyl ether; the white precipitates dissolved into the ethereal layer to give a yellow solution. By bubbling air into the separated ethereal solution for 30 min, the yellow color of the solution completely disappeared with a formation of white precipitates, which were collected by filtration, washed with ethyl ether and dried under vacuum to give 0.684 g (1.32 mmol) of triphenylmethyl peroxide (52.5% yield), identified by the superimposability of its infrared spectrum with that of the authentic sample. The filtrate, after the usual work up and evaporation, afforded 0.868 g of a yellowish solid, which was then chromatographed over 38 g of silica gel (Nakarai, No. II-A, 100-200 mesh). The fractions eluted with n-hexane-benzene (85:15) gave 0.181 g (0.995 mmol) of bitropyl (39.8% yield), the identity established from its infrared spectrum as described above. From the subsequent fractions with the same eluent was obtained 0.392 g (1.17 mmol) of 7-trityltropilidene (23.4% yield), mp $167-170^{\circ}\text{C}$ (dec) (lit, mp 156°C^7); NMR, τ_{CCl_4} 2.80 (s, 15H, phenyl), 3.25 (t, 2H,

H^{3,4}), 3.81 (m, 2H, H^{2,5}), 4.72 (d of d, 2H, H^{1,6}) and 7.06 (t, 1H, H⁷); UV, $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 260 nm (ϵ , 46000), and two shoulders at 265.5 and 272 nm (lit, $\lambda_{\text{max}}^{95\% \text{ EtOH}}$ 259 nm (ϵ , 47000), 272 nm (sh) (32000)⁷).

Found: C, 93.52; H, 6.62%. Calcd for C₂₆H₂₂: C, 93.37; H, 6.63%.

The fractions with benzene as an eluent gave 0.015 g (0.084 mmol) of benzophenone (1.7% yield), identified as described above. The subsequent fractions eluted with benzene afforded 0.230 g (0.885 mmol) of triphenylcarbinol (17.6% yield), identified as mentioned above.

On the other hand, the ultraviolet spectroscopy of the aqueous layer indicated that 1.58 mmol (31.6%) of the tropylium ion remained unchanged.

Zinc Reduction of the Tropylium Ion in the Presence of the Trityl Radical. 7-Trityltropilidene was synthesized by the coupling of the trityl radical with the troyl radical produced by zinc reduction of the tropylium ion in benzene-acetonitrile. To a stirred benzene solution (18 ml) of the cyclohexadiene I (1.13 mmol) containing zinc dust (2.94 g), an acetonitrile solution (18 ml) of tropylium fluoroborate (4.50 mmol) was added, drop by drop, under a nitrogen atmosphere over a 15-min period at room temperature. The reaction mixture was then filtered; the filtrate was washed with water, dried, and concentrated to give an oily solid (0.849 g), which was then chromatographed over silica gel (70 g). Bitropyl (0.185 g, 45.3% yield) and 7-trityl-

tropilidene (0.459 g, 61.0% yield based on the cyclohexadiene I; 30.5% yield based on the tropylium ion) were eluted with 95:5 and 90:10 n-hexane-benzene respectively.

ESR Measurements. The ESR spectra were taken on a Japan Electron Optics X-band spectrometer, model JES-3BS-X, equipped with a 100 kHz field modulation unit. The evacuated sample tube to be heated was placed in a JEO Associates JES-UCT-2X quartz Dewar sleeve set in a TE₀₁₁ JEO cavity.

Acknowledgment. The technical assistance of Mr. T. Kinoshita in the ESR measurements is gratefully acknowledged.

Results and Discussion

Competitive Reduction of the Triphenylmethyl Cation and the Tropylium Ion with Zinc Powder. A competitive reduction of an equal amount (0.10 M, each) of the triphenylmethyl cation and the tropylium ion was conducted with zinc powder, which is 0.8 molar equivalent for the reduction of the total amount of the cations, in anhydrous acetonitrile in an atmosphere of nitrogen (-9~-6°C, 5min). From the crude product mixture was isolated 7-trityltropilidene (23.5% yield), along with triphenylmethyl peroxide (52.5% yield), bitropyl (39.8% yield), and benzophenone (1.7% yield) which is supposed to have resulted by decomposition of triphenylmethyloxy radical, after the usual

work-up in the air and subsequent column chromatography. These products are considered to have been formed either by coupling of the trityl and tropylium radicals or by air oxidation of the trityl radical. Thus, the product ratio of the competitive one-electron reduction of the triphenylmethyl cation and the tropylium ion is calculated to be 77.7 : 63.3. A control experiment indicated that a reaction of the trityl radical (ca. 0.04 M) with the tropylium ion (0.09 M) at -12°C for 30 min in acetonitrile gives rise to a small amount (1.9% yield) of 7-trityltropilidene; this product is supposed to have been formed by the coupling of the tropylium radical, presumably formed by one-electron transfer from the trityl radical, with the unchanged latter radical. If one takes this secondary reaction into consideration, the values of the product ratio described above should become somewhat larger.

Although a more detailed study seems to be needed for an accurate estimation of the relative reducibility, this product ratio can be regarded as a direct evidence for the greater reducibility of the triphenylmethyl cation.

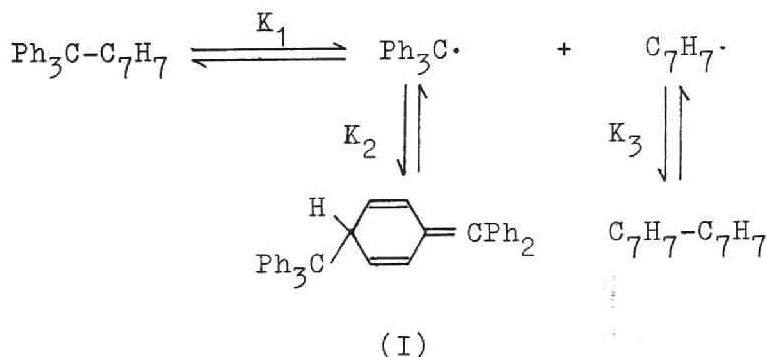
In another experiment for a synthetic purpose, 7-trityltropilidene was obtained in the better yield (61.0% yield), through the in-situ formation of the tropylium radical by zinc reduction of the tropylium ion, in the presence of the trityl radical (see Experimental).

Homolytic Dissociation of 7-Trityltropilidene. —

ESR Measurement. A degassed solution (0.1 M) of 7-trityl-

tropilidene in m-xylene gave the ESR signals of the trityl radical at 60—100°C; the signal gradually increased in intensity and became constant after 1—5 hr at 85—90°C or after 10—20 hr at 65°C. The concentrations of the trityl radical were estimated to be 3×10^{-6} — 6×10^{-5} M at 60—95°C by a comparison of the integral spectrum, recorded under overmodulated conditions (modulation width, 5.0 G), with that of a standard diphenylpicrylhydrazyl solution. The signal intensity of the trityl radical in a sample preheated at 100°C decreased when the sample was kept at lower temperatures, thus reaching the same value as that of another sample not preheated. After each measurement, no discoloration of the solution was observed, and the TLC analysis of an aliquot gave a sole spot with the same R_f value as that of the authentic 7-trityltropilidene.⁸⁾

The ESR signal for the tropanyl radical was not observed under the conditions here employed. This is most probably the result of the lowering of the concentration of the tropanyl radical due to its dimerization to bitropanyl. Since the trityl radical is also in equilibrium with the cyclohexadiene I ("hexaphenylethane"), we may assume the following equilibration scheme:



If the above scheme holds under the conditions employed, the equilibrium constant, K_1 , for 7-trityltropilidene can be calculated from Eq. (1):

$$K_1 = (b/a) \left\{ -1 + \sqrt{1 + (16b^2/K_2K_3) + (8b/K_3)} \right\} (K_3/4) \quad (1)$$

where a and b are, respectively, the concentrations of 7-trityltropilidene and the trityl radical.⁹⁾ The results are summarized in Table 1, along with the thermodynamic parameters.

Thus, in the temperature range from 60 to 95°C, the values of the equilibrium constant are in the sequence: the cyclohexadiene I > $\text{Ph}_3\text{C}-\text{C}_7\text{H}_7$ > $\text{C}_7\text{H}_7-\text{C}_7\text{H}_7$, whereas the values of ΔH and of ΔS are in the sequence: $\text{Ph}_3\text{C}-\text{C}_7\text{H}_7$ > $\text{C}_7\text{H}_7-\text{C}_7\text{H}_7$ > the cyclohexadiene I. Although the sequence of the equilibrium constant seems quite reasonable, it seems to be difficult to explain the abnormally high values of ΔH and of ΔS for 7-trityltropilidene on the basis of the

TABLE 1. EQUILIBRIUM CONSTANTS, ENTHALPY AND ENTROPY FOR THE DISSOCIATION OF 7-TRIPHENYLMETHYL-1,3,5-CYCLOHEPTATRIENE IN *m*-XYLENE

Temp. °C	Concn. of Ph ₃ C ^{a)} M × 10 ⁶	Equilibrium constant		
		Ph ₃ C-C ₇ H ₇ K ₁ × 10 ¹⁶ c)	I ^{b)} K ₂ × 10 ³ d)	C ₇ H ₇ -C ₇ H ₇ K ₃ × 10 ¹⁷ d)
60.0	2.71	1.50	1.41	2.24
65.0	4.16	3.96	1.82	4.68
70.0	8.07	18.4	2.29	10.0
75.0	7.17	19.6	2.95	20.4
80.0	17.4	53.4	3.63	39.8
83.0	24.1	213	4.17	63.2
85.0	15.8	127	4.52	81.3
88.0	41.1	691	5.18	126
90.0	25.1	360	5.69	162
93.0	50.8	1250	6.36	235
95.0	55.0	1617	6.92	309
ΔH	(kcal/mol)	50 ± 2	11 ^{d)}	35 ^{d)}
$\Delta S(60^\circ\text{C})(\text{e.u.})$		78.4	20.0	27.3

a) The initial concentration of 7-trityltropilidene was 0.1M.

b) I = 1-diphenylmethylene-4-triphenylmethyl-2,5-cyclohexadiene.

c) Calculated from Eq. (1) (see text).

d) The values for *K*'s were extrapolated from data at the other temperatures: see Refs. 1 and 9

steric and the electronic factors which were considered in the cases of genuine hexaphenylethane¹⁰⁾ and bitropyl.¹⁾ These questions remain to be elucidated in the future.

Summary

The results of the competitive one-electron reduction of the triphenylmethyl cation and the tropylium ion indicated the greater reducibility of the former cation; the ratio of the reduction-product yield of both cations was shown to be 77.7% : 63.3%. It was found that 7-triphenylmethyl-1,3,5-cycloheptatriene, the radical coupling products formed in this competitive reduction, thermally dissociates into the triphenylmethyl and troyl radicals, which are also in equilibrium with their dimers, the "hexaphenylethane" and bitropyl, respectively. From the results of ESR study at 60-95°C, the degree of dissociation and the dissociation energy of this compound at 60°C were calculated to be $2.7 \times 10^{-3}\%$ and 50 ± 2 kcal/mol, respectively.

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- 5) K. Conrow, "Organic Syntheses," Vol. 43, p. 101 (1963).
- 6) H. J. Dauben, Jr., L. R. Honnen, and K. M. Harmon, *J. Org. Chem.*, 25, 1442 (1960).
- 7) 7-Trityltropilidene was first synthesized from triphenylmethylsodium and tropylium fluoroborate by M. R. Rifi and H. J. Dauben, Jr. (M. R. Rifi, Ph. D. Thesis, p. 105, the University of Washington, 1963); we are indebted to Professor K. M. Harmon of the University of Washington for informing us of the details of Dr. Rifi's

thesis.

- 8) It has been reported that 7-trityltropilidene gave a small amount of an oily product when heated in refluxing benzene for 4.5 days (F. R. Hunter, Ph. D. Thesis, p. 155, the University of Washington, 1966); we are grateful to Professor K. M. Harmon for informing us of the details of Dr. Hunter's thesis.
- 9) The values of K_2 and ΔH for the dissociation of the cyclohexadiene I were taken to be, respectively, 2×10^{-4} (25°C) and 11 kcal/mol in benzene.^{3b)} The values of K_3 and ΔH for the dissociation of bitropyl were evaluated by means of ESR spectroscopy following the method of Vincow and his collaborators;¹⁾ K_3 for a 2.9 M solution of bitropyl in m-xylene, 1.2×10^{-13} (126°C); ΔH (the average value for three runs), 34.5 kcal/mol (124.5-152.0°C) (lit, ΔH for a neat sample, 35 ± 1 kcal/mol¹⁾).
- 10) a) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley & Sons, New York (1955), Section 7.6.
b) S. W. Benson, J. Chem. Educ., 42, 502 (1965).

Chapter 10 General Conclusion

The study presented in this thesis was initiated with an intension to clarify some mechanistic aspects of the one-electron reduction of stable carbonium ions, which has not been investigated systematically so far.

To begin with, a systematic scrutiny was made into the inorganic reducing agents, i.e., metals and metallic ions, with various degrees of reducing power. Among these reagents, Cr(II) was chosen as a reductant applicable for a kinetic investigation on the reducibility of stable carbonium ions in aqueous solution by the use of a flow method. This is the first example reported on a kinetic study of the one-electron reduction of carbonium ions in solution. To the cations which are unstable in aqueous media, a method of the competitive reduction with zinc was applied. With respect to the zinc reduction, the mechanism of initial one-electron transfer was confirmed with the radical trapping technique.

The methods described above were applied to the stable carbonium ions of the triphenylmethyl, tropylium, and cyclopropenium systems with a variety of substituents. The results were compared with other measures for the ability of cations to receive one electron, such as the charge-transfer transition energy with a standard electron donor and the polarographic half-wave potential. It was thus

concluded that these chemical methods are successfully applicable for the estimation of the relative "one-electron" reducibility of the carbonium ions in solution. It was also indicated that thus obtained chemical reducibility exhibits a linear free-energy relationship with pK_R^+ values of the cations.

Finally, the cross-coupling product of the radicals formed by the reduction of the triphenylmethyl cation and the tropylium ion was shown to undergo a reversible homolytic dissociation upon heating. The ESR study enabled us to estimate the dissociation energy of the central carbon-carbon bond.

The results described in each chapter are summarized below:

In Chapter 2 is presented the results of an examination into the reactivity of the tropylium ion and the triphenylmethyl cation toward various inorganic reductants. The high reducibility of the tropylium ion was indicated by the formation of bitropyl even with the reductants of low oxidation potentials, such as Hg (oxidation potential, -0.789 V) and Fe(II) (-0.771 V). The triphenylmethyl cation was shown to be even more readily reduced than the tropylium ion, in agreement with the polarographic half-wave potentials of these cations, the ionization potentials of the corresponding radicals, and the results of HMO calculations.

In Chapter 3 is given a proof, obtained with a radical

trapping technique, for generation of the radical species (the tropyli radical) during the course of metal reduction of the tropylium ion. Zinc was employed as a representative metal reductant. It was also observed that the radical trapping product, N-t-butyl-N-tropylnitroxide, readily rearranges to α -phenyl-N-t-butylnitron under the given reaction conditions.

Chapter 4 is concerned with a mechanistic study on the chromous-ion reduction of the tropylium ion in acidic aqueous media. From the effects of various types of added anions upon the reduction rate, it was proposed that the chromous-ion reduction of the carbonium ion proceeds not by the direct interaction of both reagents but through an electron-transfer bridge, i.e., by a mechanism analogous to the "inner-sphere mechanism" known in the field of inorganic metal-complex chemistry.

In Chapter 5 is described the results of a kinetic study on the reduction of some substituted tropylium ions with Cr(II). The reducibility of the cations, as expressed by $\log k_2$ of the chromous-ion reduction, was found to be linearly correlated with the transition energy ($\nu_{CT \max}$) of the charge-transfer band with pyrene as a standard donor, and also with the polarographic half-wave potential of the cations. From these observations, it was concluded that $\log k_2$ obtained by this method can be successfully used as a relative measure for the electron affinity of the stable carbonium ions in solution.

This method was further extended to the reduction of a series of substituted phenyltropylium and n-alkyltropylium ions, as is described in Chapter 6. In the former case, a good linear free-energy relationship was observed with pK_R^+ and with Hammett's σ_p ($\rho = +1.31$), rather than with Brown's σ_p^+ , reflecting the twisting of the planes of the phenyl and tropylium rings. On the other hand, a slight rate-alternating effect of the n-alkyl group was observed in the latter case.

In Chapter 7 is described the results of an exploration of another method for the estimation of the reducibility, applicable for the hetero-atom substituted tropylium ions which are unstable in aqueous media. The competitive reduction conducted in anhydrous acetonitrile with zinc was found to be a satisfactory method suitable for the present purpose; its validity was confirmed from the comparison of the results with those obtained with the chromous-ion reduction method. The relative reducibility thus obtained was also found to be linearly correlated with $\mu_{CT \max}$. Furthermore, the effect of hetero-atom substituents directly bonded to the seven-membered ring upon the reduction rate was found to be expressed by a Hammett-type correlation. The sensitivity of the reactivity to the change in ring substituents was shown to be much greater than in the case of substituted phenyltropylium ions.

In Chapter 8 is described an extension of the kinetic study on the chromous-ion reduction to the cations of the

cyclopropenium system. The relation of $\log k_2$, for the reduction of the tropylium and cyclopropenium ions, with pK_R^+ values was found to be expressed by independent two straight lines with regard to each carbonium-ion system. On the other hand, the $\log k_2 - \nu_{CT \max}$ correlation was shown to be linear regardless of the carbonium-ion structure, thus, further confirming the validity of the chromous-ion reduction method for the estimation of "one-electron" reducibility with regard to the wider range of the carbonium-ion structures.

In Chapter 9 was presented the results of a competitive reduction of the triphenylmethyl cation and the tropylium ion, and of an ESR study on the homolytic dissociation of 7-triphenylmethyl-1,3,5-cycloheptatriene, which was produced by the cross-coupling of the triphenylmethyl and tropyl radicals formed by the competitive reduction. Owing to the considerable stability of the generated radicals, this compound was found to dissociate readily at $>60^\circ\text{C}$ to the extent observable with ESR spectroscopy. From the temperature dependency of the equilibrium constant for dissociation, ΔH for the cleavage of the central carbon-carbon bond was estimated to be 50 kcal/mole.

This thesis has described a fundamental study concerning the one-electron reduction of the carbonium ion, which is obviously one of the most essential chemical transformations for the generation of the organic radical.

The extension of the present study will lead to the various interesting subjects in the fields of both theoretical and applied chemistry. Some of such expected subjects are as follows: the exploration of new substituent constants explicitly applicable to the one-electron reduction of the carbonium ion to the radical, the investigation into the photochemical electron transfer through the formation of the carbonium-ion charge-transfer complex, the synthetic study of new types of hydrocarbons from the divalent carbonium ions containing the cycloheptatrienyl and/or cyclopropenyl unit, by the use of the intra-molecular coupling of the radicals formed by the one-electron reduction, the application of the present reaction to an initiation of the radical polymerization, and so on.

ACKNOWLEDGMENT

The studies presented in this thesis are the summaries of the author's work carried out during 1967-1973 at the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University.

The author would like to express his sincerest gratitude to Professor Kunio Okamoto for his continuous guidance and encouragement during the course of this study. Grateful acknowledgment is also made to Professor Haruo Shingu for his academic stimulations and encouragement.

The author is also grateful to Dr. Yoshihisa Matsui of Shimane University for polarographic measurements.

It is the author's great pleasure to thank Mr. Susumu Tsukada, Mr. Osamu Murai, Mr. Osamu Sakaguchi, Mr. Akira Hitomi, Mr. Masami Fujimori, and Mr. Sumio Yasuda, for their valuable collaboration devoted to the present work.

Finally, the author wishes to thank his wife, Yoko, for her help in correcting and typing the manuscript.

Koichi Komatsu

December, 1973

